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THE CORDIERITE-ANTHOPHYLLITE MINERALIZATION AT BLUE HILL, MAINE, AND ITS RELATION TO SIMILAR OCCURRENCES

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Introduction.—When Mr. D. G. B. Thompson went to the Blue Hill mining district in 1923, in search of material and specimens for his Bachelor's thesis,[1] he did so with small hope of finding many new and important facts. The district which has produced a few million pounds of copper, but which now has been idle for many years is mentioned in Dana's "System of Mineralogy" (p. 1054) as a locality for many minerals among them pyrite, chalcopyrite, chalcocite, cuprite, bornite, tetrahedrite and arsenopyrite. Later the district was described in the Penobscot Bay Folio,[2] in which publication the main geological features of the region are also elucidated. A few years later the Blue Hill region was described in more detail in a bulletin of the U. S. Geological Survey.[3]

General Geological Features.—The Ellsworth schists of the Penobscot Bay Folio form at Blue Hill a mass projecting into granite, and having a width of three to four miles. They are beyond all doubt of sedimentary origin and the sandy or argillaceous beds have been transformed into a quartz-chlorite-biotite schist by a metamorphism which antedated the intrusion of the granite. The age of the schists is possibly pre-Cambrian, more probably Cambrian. After the metamorphism they were introduced by a granite which shows no dynamic metamorphism and which is considered of Silurian or Devonian age.

The ore deposits occur from one quarter to one mile from the contact and form lenticular masses of pyritic ore which grade into the schist. Professor W. H. Emmons regards them as having been formed during the Cambrian or pre-Cambrian period of igneous activity which followed the deposition of the Ellsworth sediments and thinks that they have been metamorphosed, dynamically, before the intrusion of the granite. Of this

post-Ellsworth and pre-Silurian igneous activity which resulted in the volcanic Castine series and some smaller associated intrusives there is no evidence in the Blue Hill district.

Type of Mineralization.—When Mr. Thompson's specimens were examined in the petrographic laboratory of the Massachusetts Institute of Technology, it was soon found that cordierite was an abundant and characteristic mineral. The ores are indeed a replacement of the schist in which they form lenticular bodies. The schist in this district contains quartz, biotite and chlorite as principal constituents. By replacement in the schist large quantities of cordierite and more or less anthophyllite have been formed together with additional biotite; there is also in places aggregates of apatite, developed at the same time as the rest of the mineralization. The cordierite is frequently altered to sericitic aggregates. The metallic minerals include magnetite, pyrite, pyrrhotite (with some pentlandite), chalcopyrite, molybdenite and some sphalerite, rarely galena.

This type of mineralization now found for the first time in America was formed at a high temperature, and I believe there can be no reasonable doubt that it was produced by emanations from the granite which outcrops in the close vicinity. It is characterized by an abundance of introduced magnesia, in biotite, cordierite and anthophyllite, and I can see no reason to connect it with far distant Castine eruptives. There is little evidence that the deposits have been dynamometamorphosed by a pre-granitic compression. There may be some curved and corrugated pyrite streaks as stated by Emmons but such may be formed during the stresses accompanying the granite intrusion, or may simply be replaced, old corrugations. Veinlets of chalcopyrite and pyrite replacing the schist show no crushing and compression.

The deposits are, therefore, confidently diagnosed as caused by emanations from the granite which contained Fe, Mg, S and SiO_2. That the granite has exerted contact metamorphism on the schist is proved by several occurrences of andalusite described in the literature from near the contact.

Similar Deposits in the United States.—Cordierite, a silicate of Al, Mg and Fe, occurs at a number of places in this country. In the West, for instance, cordierite-hornfels has been described by F. C. Calkins.[4] A few other localities are mentioned from the Eastern States. For instance, at Brimfield, Mass., and Richmond, N. H. (Danna's "System of Mineralogy"), where the combination cordierite, anthophyllite, pyrite and talc is said to occur. On the whole it is rare and in no place, except at Blue Hill, is there any important metallization connected with the mineral.

Anthophyllite, the rhombic iron-magnesia amphibole is also of comparatively rare occurrence.

Similar Deposits Elsewhere.—In Europe there are, of course, many occurrences of cordierite. In most cases the mineral is formed as the result

of igneous metamorphism. In places it is found in igneous rocks such as pegmatite or andesite. In some localities it is connected with strong sulphide mineralization, usually chalcopyrite, pyrite and pyrrhotite. One of these is at Bodenmais, Bavaria, where the ore forms lenticular masses in a gneiss, near the granite contact. On basis of the detailed work of Lehman and of Weinschenk this ore body was intrepreted by Bergeat[5] as "injected sulphides" and his opinion of the mode of origin is as follows: "The relations at Bodenmais force us to the view that there the injected magmatic emanations were associated with great masses of metals and sulphur which had been concentrated at the periphery of the granite and that these masses solidified in the exfoliated schists." In the same publication he included in this type of ore deposits several more or less obscure ores of Scandinavia and Finland, like those of Fahlun, Bersbo, Riddarhyttan, Långfall and Orijärvi, emphasizing, however, that the conditions were not as clear here as at Bodenmais.

Since that time much competent work has been done on the latter deposits, principally by Per Geijer and Pentti Eskola. At all these places the geological relations are more or less obscure, because the rocks in which the ores and the cordierite-anthophyllite gangue occur are leptites and amphibolites of somewhat doubtful origin.

In 1914, Eskola[6] in a memoir of great merit came to the conclusion that the ore deposits and the rocks of the Orijärvi district owe their composition to a "pneumatolytic metamorphism." Vapors or solutions carrying iron, magnesia and silica soaked into the leptite from the oligoclase granite. These vapors also contained heavy metals and sulphur. The result was a replacement of the leptite by cordierite, anthophyllite, quartz and sulphides. He rejects the view that the ores might have been caused by an actual injection of sulphide magma and places them in the metasomatic group of deposits.

Later, in 1923, Geijer[7] states regarding the similar deposits of the Riddarhyttan district, Sweden, that many similarities are apparent between the Källfall type of magnetitesulphide deposits at Riddarhyttan and the sulphide ores of the Fahlun and Orijärvi type. In all cases the ores are accompanied by cordierite, anthophyllite and biotite, and have resulted from the replacement of leptite by vapors containing iron, copper, magnesia and sulphur. The ores form transitions into the leptite country rock and are not filled fissures or injected dikes. He characterizes the process as a "magnesia metasomatism."

Conclusions.—It needs scarcely to be emphasized how entirely similar the described occurrences from Fenno-Scandia are to the deposits at Blue Hill. At the latter place the conditions are, however, much clearer for the sedimentary nature of the schists and the magnesia-iron-copper metasomatism are perfectly plain. A large number of occurrences of "injected

magmatic sulphides" thus resolve themselves into problems of replacement by mobile liquid or gaseous emanations in quartz or silicate rocks.

Such magnesian metasomatism can probably only be carried out under conditions of very high temperature. We find some indication of this in the common presence of biotite in altered wall rocks of certain high temperature veins such as those Knopf has described from Alaska, and other observers have noted from Rossland, B. C. The scarcity of such ores of this type in the West is doubtless related to the fact that the intrusions there took place in a higher zone with less extreme temperatures.

Such injections as Bergeat had in mind are similar to those which Spurr[8] has designated as "ore magmas."

It is a question whether this nomenclature is correct and should be adopted. The word magma has a perfectly definite meaning. It describes a liquid of high temperature consisting of a solution of complex silicates in each other, perhaps with admixed oxides and always containing a certain quantity of dissolved volatile matter. I cannot find a definition of "ore magma" in Spurr's book. It is said to be concentrated, viscous, pasty, but from other passages it may apparently be composed of almost any product of differentiation of the normal parent magma. It would follow of course that silica, iron oxides, mixed magmatic liquids, and volcanic gases may be referred to as "ore magmas" if metallic deposits are formed by their solidification, crystallization or sublimation. I submit that logical usage demands that the term "magma" be restricted to the above definition. Surely a volcanic gas consisting of sodium and iron chlorides should not be called an "ore magma," or even a "magma." When differentiation has proceeded to the point where only one component or several similar components remain the term magma should be dropped. One may properly speak of quartz, or iron ores, or gases *of magmatic origin.*

[1] Examination of the Blue Hill, Maine, Mining District. Submitted in Partial Fulfilment of the Requirements for the degree of Bachelor of Science, Mass. Inst. Technology, 1923.

[2] G. O. Smith, E. S. Bastin and C. W. Brown; *U. S. Geol. Survey Geol. Atlas*, Penobscot Bay Folio (No. 149), 1907.

[3] W. H. Emmons: Some Ore Deposits in Maine. *Bull.* **432,** *U. S. Geol. Survey*, 1910.

[4] W. H. Emmons and F. C. Calkins: Geological and Ore Deposits of the Philipsburg Quadrangle, Mont. *Prof. Paper* **78,** *U. S. Geol. Survey*, 1913.

[5] Stelzner-Bergeat: *Die Erzlagerstätten*, II, pp. 966–967, 1905–06.

[6] Pentti Eskola: On the petrography of the Orijärvi region, *Bull. Comm. geol.*, Finlande, No. 40, p. 259.

[7] Per Geijer: *Riddarhytte malmfalt.* Edited by the Dept. of Commerce and the Geological Survey of Sweden, Stockholm, 1923, p. 122.

[8] J. E. Spurr: *Ore Magmas*, New York, 1923.

GEL REPLACEMENT, A NEW ASPECT OF METASOMATISM

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Introduction.—Perhaps the title of this paper is too brief. It should read: Replacement of rock-forming minerals and sulphides by gels; a new aspect of metasomatism in solid rocks.

The petrographer understands by replacement, or metasomatosis the process by which one mineral is transformed into another by practically simultaneous solution and deposition. It is effected by solutions moving along capillary or sub-capillary openings. At no stage are there any openings visible under the microscope. Replacement goes on in all rocks, at all times when they are permeated by liquids, or gases. Near the surface it results in the change of feldspars, ferromagnesian silicates of igneous rocks into chlorite, sericite, calcite, quartz or similar minerals. Analogous processes go on in sedimentary rocks. At higher temperatures rocks are replaced by minerals stable under the new conditions; for instance, limestone penetrated by gaseous or liquid emanations from magmas develop garnet, wollastonite, epidote, etc.

I believe that in solid rocks replacement proceeds by equal volumes,[1] that is, the volume of the new mineral is the same as that of the mineral removed. Under usual conditions the resulting mineral is a crystalloid, with or without crystalline outlines. The new mineral I would call the *metasome* or the guest, contrasted to the original mineral which would be called the host. When the metasome assumes its own crystal form it is called a *metacryst.*

These statements are based on empirical observations. Little has been done in providing an adequate chemical explanation for the phenomena of replacement. It is evident that they belong in the category of capillary chemistry intimately related to the boundary of phases. The chemical results cannot as a rule be expressed in the simple formulas ordinarily used and the phase rule does not hold.

Gel Replacement.—In less common cases the new mineral—the guest—is deposited in the colloid state as a gel, and I have reason to think that this form of replacement happens more frequently than has hitherto been supposed. The gel has often a more or less clear colloidal or *colloform* structure expressed by curved, reniform or spheroidal form.[2] It is very likely to be converted into a crystalline often radially fibrous aggregate sooner or later after its deposition, that is, it becomes a *metacolloid.* Let it be understood that I am not speaking of colloform gels deposited on the walls

of fractures or in loose materials, or in sea water, but exclusively of processes going on in solid rocks.

For instance, a limestone may be replaced by a silica gel, hardening after some time to opal or becoming transformed very shortly after its deposition into the fibrous metacolloid which we know as chalcedony.

Conditions of Gel Replacement.—Gel replacement operates in general at medium to low temperatures, probably not above 300°C. It occurs at the surface and to a depth of perhaps many thousand feet. Solutions or sols moving in capillary or subcapillary openings form the medium of attack and precipitation. These liquids attack the matrix and dissolve it or decompose it. As the equilibrium is disturbed the gel precipitates by the action of an electrolyte on the sol, or by interaction of two differently charged sols or by the reaction between two electrolytes. As many rocks are not easily penetrated by sols it is probable that in most cases the latter mode is active as, for instance, in the precipitation of metallic sulphides by sodium sulphide. In all cases it is probable that the reactions are governed by capillarity and adsorption, and that they do not proceed by the phase rule nor exclusively by the law of mass action. It is also probable that in many cases no chemical reactions can be written which adequately express what has taken place.

The new substance which fills the place of the dissolved or decomposed host will be a gel of high concentration. If the gel crystallizes after a while the usual concentric-fibrous texture result and there will be a contraction which finds expression in concentric open spaces or irregular cracks which afterwards may be filled by another substance. If the recrystallization takes place almost simultaneously with the deposition there may be apparent continuity and solid texture because new gel immediately fills in the fractures of the crystallizing jelly.

The resulting product may be homogeneous, as, for instance, when marcasite replaces gangue, or other sulphides; or again if the product was composed of a mixture of gels and electrolytes, the resulting crystalline mass may be a complex and intimate aggregate in which it is difficult or impossible to find any succession among the various minerals.

In soft sediments and in rocks disintegrated by oxidation concretionary forms of limonite, bauxite, barite, marcasite and many other minerals occur frequently. This too is the result of gel replacement in capillary openings and forms part of the processes known as diagenesis and weathering but these cases are not discussed specifically in this article which, as stated, deals mainly with replacements in solid rock.

Replacement by Silica Gel.—For many years petrographers have explained the occurrence of certain kinds of chert in limestone by a replacement of this kind and no doubt this view is in many cases correct. Geologists are familiar with beautiful small shells occurring in various formations which

have been transformed into chalcedonic silica with preservation of there most delicate sculpture. This too is undoubtedly a gel replacement.

The so-called siliceous oolites are a particularly convincing case of gel replacement. Here the original rock was an oolitic limestone, itself of colloid origin. Siliceous solutions have effected a complete replacement with retention of structure and the gel recrystallized to chalcedonic quartz.

In previous papers I have called attention to gel replacement of fine-grained dolomitic limestone in the immediate vicinity of ore deposits.[3]

In contrast to the crystalloid replacement which begins at numerous points in the rock by the development of individual crystals of quartz, the gel replacement proceeds like a wave uniformly replacing the limestone and crystallizing to a micro- or crypto-crystalline aggregate of fibrous silica. Retention of structure is apparently characteristic of this type of replacement. If any considerable mass of rock is replaced, pressure may easily cause collapse of the gelatinous structure.

Experimental demonstration of the replacement of calcite by gelatinous silica has been furnished by A. H. Church[4] many years ago.

The chemical explanation has been furnished by Cox, Dean and Gottschalk,[5] who showed that when a colloidal solution of silica contains carbon dioxide and allowed to act on calcium carbonate the silica is rapidly precipitated by the positively charged calcium ions of dissociated calcium bicarbonate. Without CO_2 no reaction takes place. It is evident that no equation can be written for this reaction, and that it is governed by no ordinary stoichiometric rules.

Replacement by Sulphides.—It has long been known that marcasite concretions form in soft sediments and oxidizing rocks by the process called diagenesis. The iron is undoubtedly deposited as a gel of FeS which later crystallizes to Fes_2 by the aid of simultaneously precipitated sulphur.

Later investigations have shown that a similar process may go on in solid rocks, though the chemical mechanism of the reaction cannot always be explained in detail.

In a rock from the sulphide deposit of the Iron Queen Mine, Mayer, Arizona,[6] it was found that marcasite with colloform structure freely replaces the gangue minerals as well as pyrite and sphalerite. Soon after Mr. Newhouse[7] of the Geological Department of the Massachusetts Institute of Technology, found entirely similar occurrences at Kokomo, Colorado, and in the ores of the Angangeo district, Michoacan, Mexico. Here too quartz and pyrite appeared to be replaced by marcasite with colloform structure. The process is later than the main mineralization, and it is believed that it took place below the water level and below the oxidized zone. An entirely similar case of marcasite forming below the oxidized zone at Ducktown has been examined by Gilbert.[8] He describes marcasite with typical colloform structure replacing pyrrhotite and presents excellent pho-

tographs of the altered rocks though nor referring to the colloid origin. Sphalerite is also replaced, but not pyrite and chalcopyrite. The process is explained by solution of pyrrhotite by sulphuric acid, and the action of the resulting hydrogen sulphide on ferrous-ferric sulphates. Under such conditions the result would be a gelatinous precipitate of FeS and S which would crystallize to FeS_2.

Similar occurrences of marcasite were observed by Mr. Gilbert from the Great Gossan lead of Virginia and at Rossland, B. C. Again, concentric rings of marcasite (or pyrite) were observed by W. Lindgren[9] as a replacement in an ore at Tintic in the Gemini Mine, which is believed to have been altered just below the water level. In this last mentioned ore there also occurred colloform sphalerite which replaces the solid cement of a dolomitic breccia.[11]

Colloidal deposition is also marked in the Transvaal "banket" or gold-bearing conglomerate. Here concretions of marcasite replace quartz, but the conditions were about on the border line for in the same conglomerate we also find pyrite crystals replacing quartz.[10]

In this connection attention should also be called to the well known concentric intergrowth of fine-grained galena and fibrous sphalerite with or without wurtzite from the Belgian zinc regions. This is known as "schalen blende" but its mode of occurrence is not known in detail. It surely suggests colloform deposition but was probably formed in open spaces.

Colloidal Deposition in the Veins of Cobalt, Ontario.—The replacements by sulphides so far described are mainly from the zone just below that of oxidation, where the solutions are derived from ores near the surface, but in which free oxygen is absent.

In veins formed at higher temperature gel replacement is not as common and in those formed at very high temperature they are probably absent. I remind you, however, of the probability that colloidal gold is present in many epithermal veins and that the native arsenic found as one of the latest hypogene minerals in many deposits is distinctly and characteristically colloform. My attention has lately been attracted to the very marked tendency to colloform structure among the arsenides and sulpharsenides of cobalt and nickel. Perhaps this is most marked in niccolite. We are likely to regard the Cobalt veins in Ontario as something rather unique, with their gangue of calcite and their complex mineralization of niccolite, smaltite, chloanthite, arsenopyrite, löllingite, cobaltite, rammelsbergite and many other similar minerals. However, if we glance through some such works as Hintze's "Mineralogie," or LaCroix' "Mineralogie de France" we soon find that the peculiar association of minerals and types of structure are exactly the same as those of a dozen long known European deposits. The concentric and concretionary structures are extremely common.

At Cobalt the mineralization is as well known wonderfully rich in native silver but the silver is a distinctly late, crystalloid phase. It was introduced later than the arsenides and sulpharsenides.

A careful study of the Cobalt ores have led me to believe [12] that we have here one of the most instructive examples of colloidal deposition at higher temperatures. The narrow veins stand as well known in genetic relation to a thick intrusive sheet of diabase. That the metals were derived from the diabase in the form of emanations is very evident though I cannot here detail that evidence. The veins have been described by many observers and at least six of them, Wm. Campbell and C. W. Knight, W. G. Miller, E. S. Bastin, H. V. Ellsworth and W. L. Whitehead emphasize the concretionary structure of the ores, though they do not draw the inevitable inference as to the mode of origin from this structure. The veins are considered as mesothermal or formed at intermediate temperatures probably not exceeding 250°C.

At Cobalt the deposition may be divided in three stages: 1. The filling of fissures by crystalline calcite and dolomite; 2. The replacement of the carbonates by gels of arsenides and sulpharsenides; 3. The introduction, on fissures and in replacement, of crystalloid native silver. The colloform arrangement of the arsenides and sulpharsenides becomes particularly clear on polished faces and specimens. Rounded concentric aggregates appear in the carbonates, many of them with a niccolite core covered by rounded concretionary deposits of smaltite and other minerals. Under the microscope the solid aggregates resolve into extremely intricately intergrown minerals for which it is impossible to deduce any definite succession, but they are just what would be expected from the sudden crystallization of a complex gel and not from a succession of replacements. I advance with considerable confidence the view that the arsenides and sulpharsenides are a gel replacement of the older crystalline carbonate filling.

It is obviously difficult to explain the chemistry of such a complex process but if I may be allowed I shall draw a rude outline of what I believe has taken place.

The carbonate filling was affected by heated waters of uncertain origin and was completed before the next stage began. This second stage consisted in the introduction of mobile solutions emanating from the cooling diabase. They may have been mixed with more or less water of magmatic or meteoric origin.

They consisted of the chlorides of cobalt, nickel and iron, and were mixed with arsenic sulphide (colloidal?) and hypogene sulphides or alkaline sulphides. The immediate precipitation was inhibited for the time by the acid condition resulting from hydrolysis of the ferric chloride. The solutions attacked the country rock—diabase or argillite—slowly or not at all while an intense reaction was set up as soon as the encountered carbonate

filling. The solutions penetrated the granular carbonates easily and completely and attacked the calcite vigorously. This resulted in the solution becoming neutral or alkaline and the sulphides were precipitated together with the arsenate as a gel of complex composition which took the place of the dissolved calcite and assumed the typical concretionary form. Needless to say the carbon dioxide set free must have played an important part in the system.

The complex gel was almost immediately transformed into crystalloids resulting in the mixture of minerals which we now find. The crystallization was accompanied by contraction and fissuring but the spaces were immediately filled by calcite and new gel so that the result was a compact and almost solid vein. Because the crystallization followed so closely on the heels of the gel precipitates it is not surprising that we find places where crystals form by replacement in the country rock, but they are not abundant.

I think that the inspection of any extensive series of polished ores will convince the doubter that the veins have been formed by a process similar to that tentatively outlined.

The gel replacement in the calcite gangue sometimes extended with colloform outline into the country rock for short distance, but it proceeded here obviously under difficulties on account of the low solubility of the siliceous or argillaceous material.

I believe the silver also came from the diabase magma but, as stated, it was from the beginning a crystalloid product and not a colloidal precipitate.

In conclusion, I venture to hope that further observations will considerably extend the phenomena of gel replacement. It seems to account for many conditions which have seemed mysterious or difficult to explain.

[1] W. Lindgren: Volume changes in metamorphism. *J. Geology*, **26**, 1918, pp. 542–554.

[2] Such forms are generally speaking determined by surface tension in a viscous liquid.

[3] W. Lindgren and G. F. Loughlin: Geology and ore deposits of the Tintic district, Utah. *Prof. Paper* **107**, *U. S. Geol. Survey*, 1919, pp. 154–157; also in *Economic Geology*, **10**, 1915, pp. 225–240.

[4] *Phil. Mag., London*, 4th ser., **23**, 1862, p. 101.

[5] G. H. Cox, R. S. Dean and V. H. Gottschalk: Studies on the origin of Missouri cherts and zinc ores. *Bull. School Mines*, Univ. Missouri, **3**, No. 2, 1916, Rolla, Mo.

[6] W. Lindgren: Ore deposits of the Jerome and Bradshaw Mountains Quadrangles, Arizona. *Bulletin, U. S. Geol. Survey*, in press.

[7] W. H. Newhouse: Paragenesis of marcasite. *Economic Geology*, **20**, 1925, in press.

[8] G. Gilbert: Oxidation and enrichment at Ducktown, Tenn. Presented at New York meeting, Feb., 1924, of the American Institute of Mining & Metallurgical Engineers.

[9] *Prof. Paper* **107**, *U. S. Geol. Survey*, 1919, p. 179.

[10] H. C. Boydell: The rôle of colloidal solutions in the formation of mineral deposits. *Dissertation, M. I. T.*, 1924, p. 120.

[11] *Prof. Paper* **107**, p. 179 and fig. on p. 147.

[12] This conclusion was reached simultaneously by Dr. H. C. Boydell and the writer and is referred to in Dr. Boydell's notable dissertation on "The rôle of colloidal solutions

in the formation of mineral deposits." M. I. T., 1924. Published in Bull. Institution of Mining and Metallurgy, No. 243, 1924. Dr. Boydell, however, holds that the arsenides were deposited in a "carbonate gel."

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*MORTAR STRENGTH, A PROBLEM OF PRACTICAL STATISTICS**

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MAINE TECHNOLOGY EXPERIMENT STATION

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The expansion of science into fields requiring quantitative analysis of highly variable data has led to an increasing utilization of statistical technique. Engineering is no exception. The constantly widening use of portland cement mortar in highway, bridge and building operations has resulted in a desire for a more intimate knowledge of the effect, on its breaking strength, of the different elements entering into this mortar. Such a demand has lead directly to the necessity of a statistical analysis of the problem as the factors pertaining to it are all highly variable. Among these variables may be mentioned the size and the geological character of the sand, the strength of the cement both in and of itself and with a standardized sand, the personal equation of the operator making the test and the variability not common to two specimens made from the same materials. All of these problems and more require statistical treatment in their analysis.

The problem dealt with in this paper is the problem of the relation of the breaking strengths of mortars cured seven days and twenty-eight days. The present mortar testing regulations have established these two tests. The twenty-eight day tests are taken as final. The engineer, times innumerable, wishes for a more intimate understanding of the relation be tween the breaking strengths of the seven-day and the twenty-eight-day specimens such that he can with safety utilize his material on the basis of the short time test. A desire to solve this problem has led to the analysis here presented on data for 478 Maine sands in tension and 166 Maine sands in compression. Throughout all of the work, the tests were performed by experienced operators following the standard A. S. T. M. procedure. The relation between the 7-day and the 28-day tests in tension is shown in table I.

Study of table I shows that the variation of the 28-day test is much reduced when the 7-day test specimens are fixed in their tensile strength. Thus if reference is made to the table it is noted that those sands which break

* This paper is a brief of a bulletin appearing from the Maine Technology Experiment Station.

at a 7-day test between 220 and 240 pounds have a variation in 28-day strength of between 200 and 380 pounds. Whereas when all 28-day strengths are considered the variation is between 100 and 600 pounds or the fixing of the 7-day breaking strength has reduced the variation from 500 pounds to 180 pounds. Similar results follow when other 7-day test results are of fixed breaking strength. From these facts it is obvious that

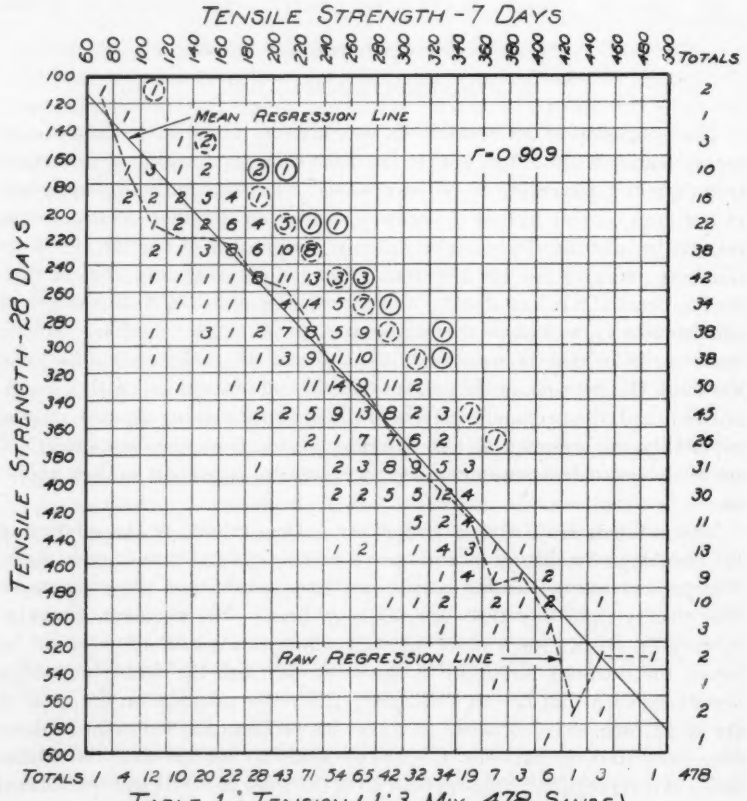

TABLE 1 - TENSION (1:3 MIX, 478 SANDS)

a high degree of relationship exists between the 7-day and 28-day tests in tension. The average 28-day breaking strength for a fixed 7-day breaking strength is shown on the table as the irregular line indicated as the "raw regression lines." The straight line shows the best fitting line to the raw data. It is clear that these results are in accord with a linear relation between the 7-day and 28-day tests.

The data surrounded by the circle indicates the specimens showing less strength at the end of 28 days curing than was found in the specimens of the same mortar cured 7 days. All sands in this table pass the colorimetric test for organic impurities. The table indicates simply normal variability of such sands and the fact that occasionally it is possible under such conditions to have 7-day specimens which will give higher breaking strengths than the other briquettes of the same sample cured 28 days.

The tables for data on tensile ratios, compression, and compressive ratios are not shown for lack of space. From the analyses of the data, however, a table may be formed presenting the interrelations of the respective 7-day and 28-day tests. Table II shows these results.

TABLE II

ANALYTICAL CONSTANTS FOR MORTARS IN 7-DAY AND 28-DAY TENSION AND COMPRESSION TESTS

KIND OF TEST	CONSTANTS		
	MEAN	STANDARD DEVIATION	COEFFICIENT OF VARIATION
7-day Tension (pounds)	251 ± 2	67.7 ± 1.5	27.0 ± 0.6
28-day Tension (pounds)	318 ± 2	79.2 ± 1.7	24.9 ± 0.8
7-day Compression (pounds)	3134 ± 45	868 ± 32	27.7 ± 1.4
28-day Compression (pounds)	4328 ± 57	1090 ± 40	25.2 ± 1.1
7-day Tensile Ratio	103 ± 1	25.4 ± 0.6	24.7 ± 0.7
28-day Tensile Ratio	95 ± 1	25.9 ± 0.6	27.3 ± 0.7
7-day Compressive Ratio	96 ± 1	25.1 ± 0.9	26.1 ± 1.1
28-day Compressive Ratio	98 ± 1	19.8 ± 0.7	20.2 ± 0.9

CORRELATION COEFFICIENTS FOR THE 7-DAY AND 28-DAY TESTS

Tension	0.909 ± 0.005	Tensile Ratio	0.853 ± 0.008
Compression	0.899 ± 0.010	Compressive Ratio	0.624 ± 0.032

Table II brings out some significant points with regard to the average 7-day and 28-day tests. It will be noted that the 7-day specimens in tension have on the average 67 pounds less breaking strength than the 28-day specimens made from the same mortar. For compression the average of the 7-day specimens is 1194 pounds less than the average of the 28-day specimens. In the Ottawa ratio the 7-day tensile ratio is on the average 8% higher than the 28-day tensile ratio. In the face of these figures it might be concluded that a cement with Ottawa sand sets up more slowly than does the same cement using a well graded sand even though the sand may be composed of quite different percentages of particles of different sizes. This conclusion is not borne out by the compression results, however, as the mean 7-day compressive ratio is 96% whereas the mean 28-day compressive ratio is 98%. These ratios further indicate that on the 28-day test Maine sands tend to be slightly less in their tensile and compressive strengths than Ottawa sand in the same test.

The standard deviations furnish the best measure of variation in breaking strength around these average tests. This constant of variation for the

7-day test in tension is 67.7 pounds. The standard deviation of 79.2 pounds for the 28-day specimens shows that the 28-day test is slightly more variable than the 7-day test. In ratio to their means, however, the 28-day test in tension is slightly less variable as shown by the coefficient of variation of 24.9 for the 28-day test in tension as compared with a coefficient of variation 27.0 for the 7-day test. The 7-day test in compression has a standard deviation of 868 pounds while that for the 28-day compression is 1090 pounds. Here again in comparison to their means the compressive strength of the 28-day test is slightly less variable than the 7-day test as shown by the coefficient of variation. The differences throughout are scarcely significant, however, indicating that in general the percentage variation around the average test is the same for the 7-day and 28-day tensions or compressions.

The standard deviations for the tensile ratios at 7 days and 28 days are practically the same, the percentage of variation for the 28-day test is slightly greater although here again the difference is undoubtedly not significant. Similarly the standard deviation of the 7-day compressive ratio is somewhat larger than that for the 28-day compressive ratio. The coefficient of variation of the 7-day compressive ratio is also larger than that for the 28-day compressive ratio. These differences are perhaps significant in view of their probable errors indicating a slightly less variation of the 28-day compressive ratios.

The correlation coefficients for the 7-day and 28-day tests are all large values indicating a fairly close relationship between the 7-day and 28-day tests. This relationship is greatest for the tension and compression on the commercial sands. The relation is also nearly as great for the 7-day and 28-day tensile ratios. For the compressive ratios the value of the correlation coefficient is less, in fact significantly less than those found for the other tests. This difference would appear to trace back to the relation of the 7-day and 28-day Ottawa tests, as the correlation between the 7-day and 28-day compressions on commercial sands is as high as any of the others tabulated. This point will be considered further when the data on cements are analyzed.

With the constants given in table II it is possible to form the suitable prediction equations to determine the 28-day strength from that found in the 7-day test. These equations are shown below.

28-day Tension = 51.5 + 1.06 (7-day Tension)
28-day Tensile Ratio = 5.6 + 0.87 (7-day Tensile Ratio)
28-day Compression = 793 + 1.128 (7-day Compression)
28-day Compressive Ratio = 50.7 + 0.49 (7-day Compressive Ratio)

From the equation given above it is possible to predict as accurately as the data will allow, the 28-day strength from the specimens cured 7 days.

The correlation coefficients are in general so high that this prediction may be made with fair accuracy. To check the accuracy of this prediction the writers took an independently determined series of 97 tests in tension and tensile ratio and applied the prediction equations to them. It was found that on the average the prediction was 13.4 pounds more for the 28-day test in tension than that actually obtained. The average error without regard to sign was 39 pounds. For the tensile ratio the average prediction was 3.6 per cent less than that actually obtained and the average error without regard to sign was 10.8 per cent. For compression and compressive ratio a series of 61 independently determined sands was available. For the specimens in compression the predicted value of the sand at the 28-day test as determined from the 7-day test was 272 pounds less than that actually obtained. The average error without regard to sign was 628 pounds. For the tensile ratio the prediction of 28-day value was on the average 2.6 per cent less than that actually obtained and the average error without regard to sign was 15.1 per cent. As might be expected from the fact that the compressive ratio shows much less correlation between its 7-day and 28-day test specimens, the error of prediction is greater in this particular series of data. On the whole, however, the prediction is fairly accurate. It is also to be remembered that the 28-day tests are not in themselves final because of the variability between the breaking strength of specimens in the same sample although cured for the 28-day period. In view of these facts it is entirely reasonable to predict the 28-day test from the 7-day test results and use them in practical mortar work.

The problem of mortar testing also takes this form. In reporting a predicted 28-day test the engineer desires to be sure that the actual 28-day test will certainly be above a definite lower limit in its strength. It is then the low limit of test likely under given conditions which the operator would like to know. The determination of such a limit involves the determination of the variation of the actual 28-day test when the 7-day test is a fixed value. The variation is given, according to the theory of error, by the standard deviation of the 28-day test times the square root of $1-r^2$. The information for this calculation is given in table II. However, on examining our independent series of data it is found that an average Lexian ratio of 1.3 exists. In other words as a practical prediction the theoretical standard deviation of the test should be increased by multiplying it by 1.3. When such a procedure is adopted the lower limit of breaking strength above which a certain percentage of the 28-day test results would be found is that shown in table III.

From table III it is noted that if prediction is made from the equations previously given, 50 per cent of the 28-day tests should be above the predicted value. Seventy-five per cent of the 28-day tests should be above the predicted value minus the constants shown under column 75. Thus if the

7-day test in tension were 210 pounds the predicted value for the 28-day test would be 275 pounds or 50 per cent of the 28-day tests should be above 275 pounds. Seventy-five per cent of them should be above 275 pounds minus 29 pounds or above 246 pounds. In like manner the limit necessary to include 90 per cent or 99 per cent of the tests may be found. Thus in the illustrated case 90 per cent would be above 275 pounds minus 55 pounds or 230 pounds, 99 per cent of the 28-day tests should be above 275 − 100 pounds or 175 pounds. The results for tensile ratios, compression and compressive ratios are similarly obtained.

TABLE III

28-DAY TEST PREDICTIONS NECESSARY TO HAVE THE GIVEN PERCENTAGE OF ACTUAL 28-DAY TEST RESULTS ABOVE THE PREDICTED VALUE, THE PREDICTION BEING MADE FROM THE 7-DAY TEST RESULTS

	Percentage of actual 28-day tests above predicted value			
KIND OF TEST	50	75	90	99
Tension (pounds)	Predicted value	—29 pounds	—55 pounds	—100 pounds
Tensile ratio	Predicted value	—11.7%	—22.6%	—40.8%
Compression (pounds)	Predicted value	—416 pounds	—801 pounds	—1447 pounds
Compressive ratio	Predicted value	—13.5%	—26.1%	—47.1%

In way of conclusion it may be said that the results of this study indicate that the factors determining the strength of mortar at the end of the 7-day period of curing compared with those determining strength at the end of the 28-day period of curing are sufficiently alike to make possible the prediction of the 28-day breaking strength from the 7-day breaking strength. The error of such a prediction is on the whole not excessive.

SKEW-GROWTH CURVES[1]

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Read before the Academy November 12, 1924

In an earlier paper[2] we have pointed out that if, in the general growth curve

$$y = \frac{k}{1 + me^{a_1x + a_2x^2 + a_3x^3 + \ldots\ldots + a_nx^n}}, \qquad (1)$$

the exponent of e be cut off at the cubic term, appropriate values of the constants will give a single cycle growth curve which is unsymmetrical or skew about the point of inflection. We gave by way of illustration a theoretical case of such a skew-growth curve, but have not hitherto published any ex-

ample of the actual fitting of this curve to observational data on growth asymmetrically distributed about the point of inflection. The wide applicability of the general curve (1) to symmetrical population growth has been demonstrated.[3] It seems desirable now to show the ability of the curve to deal with phenomena of skew growth. Hitherto observational growth series which were plainly skew have been graduated (if graduated at all) either by a process of fitting two or more curves to different parts of the observed

TABLE I

GROWTH OF MALE ALBINO RAT. (DONALDSON'S DATA)

AGE IN DAYS	OBSERVED WEIGHT IN GRAMS	CALCULATED WEIGHT BY OUR EQUATION I	AGE IN DAYS	OBSERVED WEIGHT IN GRAMS	CALCULATED WEIGHT BY OUR EQUATION I
10	13.5	14.1	70	106.3	103.8
11	13.3	14.5	73	113.8	110.7
12	14.8	15.0	76	121.3	117.6
13	15.3	15.5	79	128.2	124.3
14	15.2	16.1	82	135.0	130.9
15	16.5	16.7	85	143.8	137.4
17	17.8	17.9	88	148.4	143.7
19	19.5	19.3	92	152.3	151.7
21	21.2	20.8	97	160.0	161.2
23	22.9	22.4	102	168.8	170.0
25	25.3	24.2	107	177.6	178.1
27	27.4	26.1	112	183.8	185.5
29	29.5	28.2	117	191.4	192.2
31	31.8	30.5	124	197.3	200.6
34	34.9	33.2	131	202.5	208.1
37	37.8	38.3	138	209.7	214.5
40	42.2	42.7	143	218.3	218.6
43	46.3	48.6	150	225.4	223.7
46	50.5	52.8	157	227.0	228.2
49	56.7	58.3	164	231.4	232.1
52	62.5	64.2	171	235.8	235.7
55	68.5	70.4	178	239.4	238.9
58	73.9	76.8	185	239.8	241.9
61	81.7	83.4	216	252.9	252.7
64	89.1	90.1	256	265.4	264.4
67	99.3	97.0	365	279.0	279.6
			Root mean square deviation	...	4.96

series and then welding the separate curves together where they overlap, or by attempting to make a symmetrical curve fit obviously skew material. One or the other of these plans has been followed by Hatai on Donaldson's data,[4] and by Robertson[5] variously. Aside from the mathematical inelegance of such procedures, in the particular case of skew-growth data the fits obtained have in some cases been grotesquely poor.

We present here four examples of skew-growth curves fitted with the cubic form of (1). These are: (*a*) The growth in weight of male albino rats from 10 days of age on (data from Donaldson, *loc. cit.*, pp. 108–109); (*b*) the growth of female albino rats from 10 days of age on (data from Donaldson, *loc. cit.*, pp. 110–111); (*c*) the growth in weight of *Cucurbita pepo* (Anderson's data from Robertson, *loc. cit.*, p. 74), (*d*) the growth in length of the regenerating tail of the tadpole (data from Durbin[6])

TABLE II

GROWTH OF FEMALE ALBINO RAT. (DONALDSON'S DATA)

AGE IN DAYS	OBSERVED WEIGHT IN GRAMS	CALCULATED WEIGHT BY OUR EQUATION II	AGE IN DAYS	OBSERVED WEIGHT IN GRAMS	CALCULATED WEIGHT BY OUR EQUATION II
10	13.0	14.0	70	99.8	99.8
11	12.8	14.5	73	105.6	105.6
12	15.1	15.0	76	110.4	111.2
13	15.1	15.5	79	118.8	116.7
14	15.6	16.1	82	124.7	122.0
15	17.7	16.7	85	131.5	127.0
17	19.2	18.0	88	136.0	131.8
19	20.6	19.4	92	139.8	137.9
21	22.6	21.0	97	146.3	144.8
23	24.9	22.7	102	153.1	151.2
25	27.4	24.5	107	155.8	156.9
27	30.0	26.5	112	161.4	162.0
29	31.4	28.7	117	168.0	166.6
31	32.9	31.0	124	172.6	172.2
34	35.7	34.8	131	181.0	177.0
37	39.5	38.9	138	185.0	181.1
40	43.7	43.4	143	186.6	183.8
43	47.9	48.3	150	188.2	187.0
46	52.0	53.4	157	188.0	189.9
49	57.7	58.8	164	189.5	192.4
52	62.9	64.4	171	192.2	194.7
55	68.4	70.1	178	197.0	196.7
58	74.6	76.0	185	200.0	198.6
61	78.4	82.0	192	202.2	200.5
64	85.8	88.0	365	226.4	226.9
67	96.0	93.9	Root mean square deviation	...	2.022

The equations in the several cases are:

I. *Male Rats.* $$y = 7 + \frac{273}{1 + e^{4.3204 - 7.2196x + 30.0878x^2 - 0.5291x^3}},$$

where y = weight in grams,
and x = age in hundred day units.

II. *Female Rats.* $y = 7 + \dfrac{220}{1 + e^{4.1426 - 7.6161x + 3.5065x^2 - 0.6262x^3}}$,

y and x in same units as above.

III. *Cucurbita pepo.* $y = 174 + \dfrac{5190}{1 + e^{10.3148 - 16.3399x + 8.1028x^2 - 1.6667x^3}}$,

where y = weight in grams,
and x = age in ten day units.

IV. *Tadpole tails.* $y = \dfrac{9.60}{1 + e^{4.4715 - 7.2829x + 3.3833x^2 - 0.6370x^3}}$,

where y = length of regenerated tail in number and x = age in ten day units.

The observed values and those calculated from the equations above set forth are exhibited in tables I to IV inclusive.

TABLE III

GROWTH OF CUCURBITA PEPO. (DATA FROM ROBERTSON)

DAYS	OBSERVED WEIGHT IN GRAMS	CALCULATED WEIGHT BY OUR EQUATION III	DAYS	OBSERVED WEIGHT IN GRAMS	CALCULATED WEIGHT BY OUR EQUATION III
5	267	267	16	4720	4680
6	443	399	17	4864	4850
7	658	645	18	4980	4984
8	961	1044	19	5114	5089
9	1498	1586	20	5176	5172
10	2200	2210	21	5242	5236
11	2920	2829	22	5298	5282
12	3366	3378	23	5352	5315
13	3758	3829	24	5360	5337
14	4092	4186	25	5366	5350
15	4488	4464	Root mean square deviation	...	46.1

The observations and fitted curves are shown graphically in figures 1 to 4 inclusive.

To give a concrete idea of the degree of skewness in these curves table V is presented.

The figures in the last column of the table are the significant ones. If the curves were all symmetrical their values would all be 50 per cent. In fact the highest is 38.4 and the lowest 32.5. They indicate that the departure of these curves from the symmetrical condition is substantial.

The results exhibited in the tables and graphs require little comment. All of the curves are obviously skew. The graduations are all excellent. They demonstrate the ability of our generalized growth curve to deal

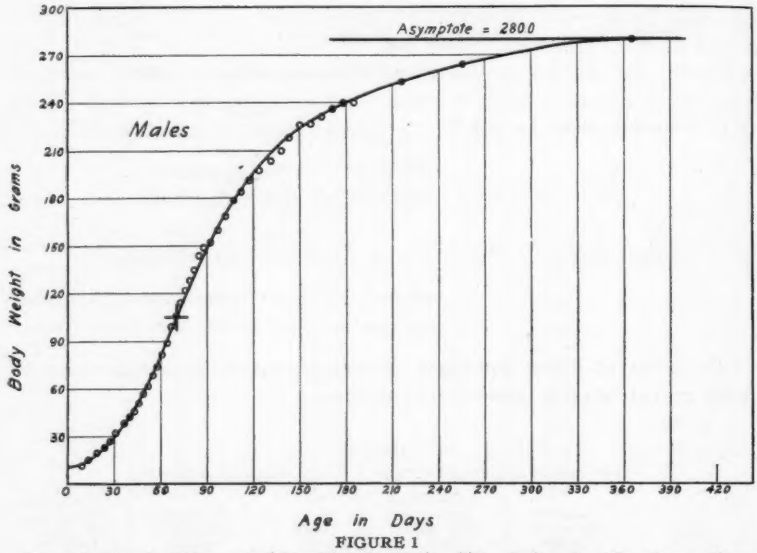

FIGURE 1

Growth of male albino rats (Donaldson's data). The circles give the observations in this and the following diagrams. The smooth curve is the graph of our equation I. The x in this and the following curves denotes the point of inflection.

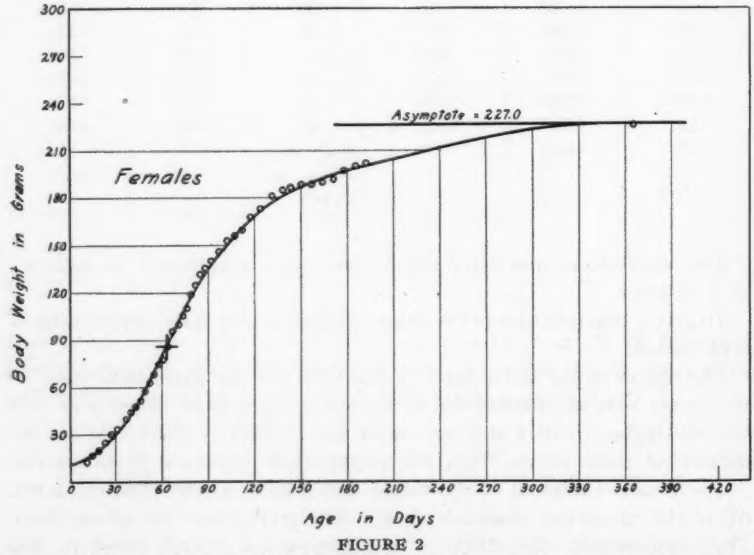

FIGURE 2

Growth of female albino rats (Donaldson's data). The smooth curve is the graph of our equation II.

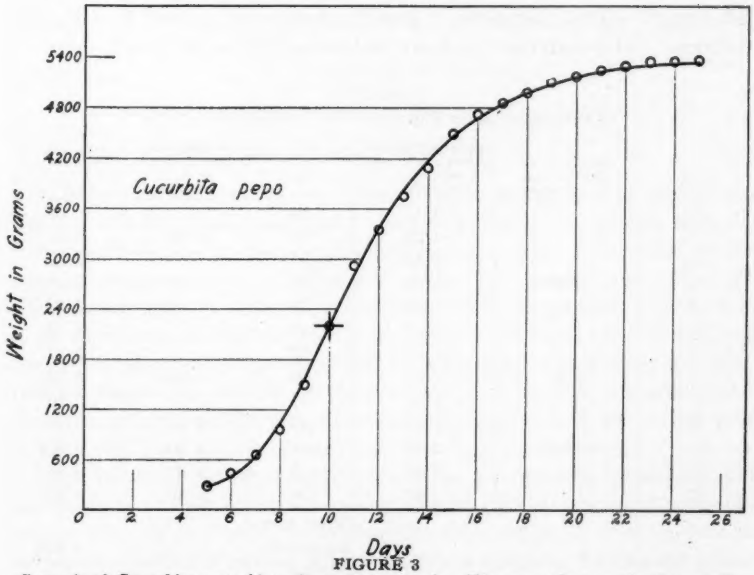

FIGURE 3

Growth of *Cucurbita pepo* (data from Robertson). The smooth curve is the graph of our equation III.

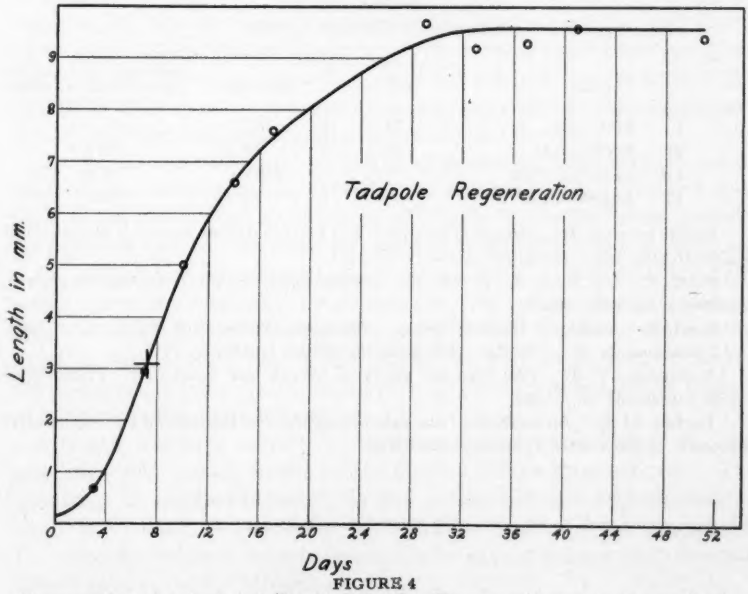

FIGURE 4

Regeneration of tadpole tail (Durbin's data). The smooth curve is the graph of our equation IV.

adequately with unsymmetrical growth phenomena as well as with symmetrical. This is all that we desire to demonstrate in this paper.

TABLE IV

REGENERATION OF TADPOLE TAIL. (DURBIN'S DATA)

DAYS	OBSERVED REGENERATION IN NUMBER	CALCULATED REGENERATION FROM OUR EQUATION IV	DAYS	OBSERVED REGENERATION IN NUMBER	CALCULATED REGENERATION FROM OUR EQUATION IV
0	...	0.11	13	...	6.37
1	...	0.22	14	6.60	6.71
2	...	0.40	15	...	7.00
3	0.68	0.68	17	7.60	7.48
4	...	1.09	19	...	7.88
5	...	1.62	23	...	8.58
6	...	2.25	27	...	9.17
7	2.95	2.95	29	9.68	9.38
8	...	3.66	31	...	9.50
9	...	4.34	33	9.20	9.57
10	5.00	4.96	37	9.30	9.60
11	...	5.50	41	9.60	9.60
12	...	5.97	51	9.40	9.60
			Root mean square deviation	...	0.196

TABLE V

SKEWNESS OF GROWTH CURVES

CURVE	POSITION OF POINT OF INFLECTION		
	ON x AXIS	ON y AXIS	PER CENT OF DISTANCE FROM LOWER TO UPPER ASYMPTOTE
I. Male rats	70.0	103.5	35.3
II. Female rats	62.3	84.5	35.2
III. *Cucurbita pepo*	9.9	2168.0	38.4
IV. Regeneration	7.3	3.12	32.5

[1] Papers from the Department of Biometry and Vital Statistics, School of Hygiene and Public Health, Johns Hopkins University, No. 111.

[2] Pearl, R., and Reed, L. J. On the mathematical theory of population growth. *Metron*, **3**, pp. 6-19, 1923.

[3] Pearl, R. *Studies in Human Biology*. Baltimore (Williams & Wilkins Co.), 1924.

[4] Donaldson, H. H. *The Rat*. Philadelphia (Wistar Institute), 1915.

[5] Robertson, T. B. *The Chemical Basis of Growth and Senescence*. Philadelphia (J. B. Lippincott Co.), 1923.

[6] Durbin, M. L. An analysis of the rate of regeneration throughout the regenerative process. *J. Expt. Zool.* 7, pp. 397–420, 1909.

CHEMICAL STUDIES ON TUBERCULIN

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Read before the Academy November 12, 1924

In his earlier work with tuberculosis, Zinsser showed that an alkaline extract of tubercle bacilli, rendered as free as possible from protein material was capable of producing a typical skin reaction of the tuberculin type in tuberculous guinea pigs. A similar skin reaction was also produced by the acid-insoluble protein fraction separated from the extract during the process of purification. At that time it could not be determined whether this was due to the adsorption of some of the so-called residue or protein-free fraction by the protein precipitate, the presence in the residue of small quantities of unprecipitated protein, or to the splitting off of an active non-protein fraction from a similarly active protein mother substance.

However, the fact that an active tuberculin, precipitable by alcohol, but free from, or at least extremely low in, protein, could be prepared, was sufficiently striking to warrant extending the observation to other bacteria to determine whether or not the phenomenon was general. During the course of subsequent experiments, Zinsser and Parker showed that extracts could be prepared by the same method from all types of bacteria investigated, including the pneumococcus, meningococcus, influenza bacillus and staphylococcus. These extracts were tested, however, by the precipitin test with specific immune sera, instead of the skin reaction, because of the difficulty of producing chronic infections in guinea pigs with these organisms. In each case the residue material precipitated specifically.

The writer undertook an investigation of these extracts from the chemical standpoint to determine if possible whether they contained protein and owed their specific serological reactions to that fact, or whether some hitherto unsuspected type of compound was capable of eliciting immune reactions.

In collaboration with Zinsser and Wayman it was at first shown that the active material precipitated by alcohol from the residue extracts, and redissolved in such concentration that mere dilution could not account for negative results, gave none of the usual color tests for protein, except the xanthoproteic reaction which occasionally appeared positive, but so slightly as to be of doubtful significance.

Nitrogen was next determined on the precipitated and dried material and was found present to the extent of from one to three per cent. The quantities of residue obtainable by the facilities at our disposal were so small as to make it impossible to determine in what form this existed. The non-nitrogenous material appeared to be, in part at least, carbohydrate since it gave a positive Molisch reaction.

In casting about for a method of attacking the problem in a manner which might hold some promise of success, we attempted to extend the investigation to a study of a similarly prepared extract of bread yeast, since this was readily obtainable in large quantities. This proved to be possible and with Tomscik we were able to prepare by a slightly modified method, considerable quantities of a complex carbohydrate, or gum, corresponding in the general method of preparation and in properties with the yeast gum or Hefegummi of the literature. This gives a specific precipitation reaction in high dilution with anti-yeast serum. It contained in some preparations less than one per cent of nitrogen and because of various considerations we felt reasonably sure that it was the carbohydrate itself which was specifically active.

During the course of these experiments, Heidleberger and Avery's work appeared, in which a similar complex carbohydrate was isolated by them from Type II Pneumococcus cultures, which also gave a specific precipitin test in extremely high dilutions.

With the experience gained in the yeast work, and with the additional aid of Heidleberger and Avery's methods, an investigation of the nature of the active material of the tuberculin is now under way. Specific precipitating sera prepared by injecting rabbits with dead tubercle bacilli are now available, and while in the case of the earlier work on tubercle extracts, to which reference has been made, the skin test alone was used as an indication of activity, both tests are now being run in parallel. While it was assumed that the same component of the tuberculin was responsible for both types of reaction, this has apparently proved not to be the case. It has been possible to obtain a fraction of tuberculin containing about one per cent nitrogen, giving a specific ring precipitin test in dilutions up to 1–400,000 with immune serum, and yet without any ability to produce a skin reaction in concentrations corresponding roughly to highly potent quantities of the original tuberculin. This fraction contains carbohydrate and is apparently comparable to the yeast gum, and to Heidelberger and Avery's pneumococcus preparations.

On the other hand, a second fraction has been separated, giving a specific precipitin reaction in low dilutions only, but producing a specific skin test in tuberculous animals in quantities equivalent to active concentrations of tuberculin. This fraction gives a strong biuret reaction in concentrated solutions, but it is not yet possible to say whether the material is even moderately pure or not.

One may perhaps suspect that the substance producing the tuberculin action will prove to be either protein or some protein split product, for while the evidence in the literature is conflicting, it seems to have been pretty well shown, and our own experiments have confirmed the fact, that proteolytic enzymes destroy the active material rather quickly. On the other

hand we have been able to show that the specific precipitable material of the tuberculin, like that of the yeast, is resistant to the action of proteolytic enzymes, and Heidleberger and Avery have demonstrated the same fact for their pneumococcus preparations.

Work on both these fractions is being continued in our laboratory to the end of clearing up their chemical nature and arriving at an understanding of the part each plays in the disease processes.

ON SCATTERED RADIATION DUE TO X-RAYS FROM MOLYBDENUM AND TUNGSTEN TARGETS

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Communicated December 5, 1924

In notes recently published in these PROCEEDINGS experiments performed in our laboratory have been described in which the spectra of secondary x-radiation have been examined by an ionization x-ray spectrometer. The curves representing the ionization currents as functions of the glancing angles of incidence of the rays on the calcite reflecting crystal contained sharply marked peaks representing scattered radiation from the secondary radiator having wave-lengths equal to those of the primary rays to within the limits of error of the measurements, but no *peaks* appeared indicating radiation comparable in intensity with the above scattered radiation and having wave-lengths corresponding with Professor A. H. Compton's interesting and important theory of single electron scattering.

Recently we have repeated some of these experiments with two important modifications in the apparatus and have found evidence of radiation agreeing very well with the equation

$$\Delta\lambda = 0.024\ (1 - \cos\theta), \qquad (1)$$

which Professor Compton deduced from his theory.

Figure 1 on page 381 of the September number of the *Proceedings of the National Academy of Sciences* represents the general arrangement of the apparatus. No large masses lay near the secondary radiator and x-ray tube except the unavoidable lead plate fastened against the brick wall. The most important changes in the spectrometer are as follows: (*a*) Instead of employing a water-cooled molybdenum target tube with a large bulb blown in it, we used in some experiments a water-cooled molybdenum target sealed into a glass tube of approximately uniform diameter throughout. This tube was about 3 cm. in diameter and its walls were made

somewhat thinner opposite the target than elsewhere in order to reduce the absorption of the rays by the glass. Professsor A. H. Compton described a similar x-ray tube in his papers and it seems admirably adapted to the investigation of the spectra of secondary radiation, not only on account of its thin walls but also because the secondary radiator can be placed much closer to the target than with a commerical x-ray tube. (*b*) We constructed a Soller[2] multiple slit system by placing a number of straight, very thin steel springs parallel to each other so as to form fourteen different slits side by side. The breadth of each slit amounted to about 0.7 mm. and the length to 50 cm. In order to reflect the rays coming through all of the slits at the small glancing angles of incidence ($6°-7°$) we had to use a calcite crystal more than 9 cm. long. The x-ray tube of small diameter and the multiple slit system very greatly increased the intensity of the secondary radiation. This has two distinct advantages. Firstly: the spectrometer possesses a much better resolving power and secondly, we could use much smaller secondary radiators. The latter proved to be of considerable importance in investigating the Compton effect for if the secondary radiator has a large volume the rays from the target strike different parts of it at different angles and according to the preceding equation (1) the shifted radiation coming from different points of the radiator and passing through the slit system will have different wave-lengths. All the points of the secondary radiator contribute to the unshifted rays producing intense radiation that lies in a relatively narrow portion of the spectrum. The shifted radiation, however, having a great variety of wave-lengths is drawn out into a broad band. The relative intensity at any point in this band is much smaller than it would be if the secondary radiator had a very small volume and all the secondary rays examined made very nearly the same angle with the primary rays.

With this apparatus, we have examined the secondary radiation coming from a large number of secondary radiators composed of different chemical elements (lithium and elements of higher atomic weight). We placed these radiators in different positions near the tube, sometimes so that only a very narrow beam of primary rays struck them and sometimes so that the primary rays made a great variety of angles with the secondary radiation. In every case narrow peaks appeared on the curves representing scattered radiation with unshifted wave-lengths. The intensity and distribution of the radiation having somewhat longer wave-lengths than the primary depended upon the size and exact position of the secondary radiator. If this radiator was placed so that only a narrow beam of primary rays produced the secondary rays, a well-marked peak somewhat broader than the unshifted peak appeared and this peak changed its position in the spectrum in substantial agreement with the preceding equation (1). If the secondary radiator was so placed as to utilize a large number of primary

rays coming at different angles to the secondary the curves showed a sharp peak corresponding to the unshifted radiation with a broad shelf alongside of it, similar to some of the curves already published representing previous experiments. The fact that the radiation of shifted wave-lengths depends so much upon exact experimental conditions should not be taken to mean that the Compton Effect itself is very variable. It furnishes rather excellent confirmation of equation (1), for, in those cases in which we did not observe a shifted peak but a broad shelf, this equation indicates that the radiation should be drawn out into a broad band, no part of which is very intense as compared with the unshifted radiation.

In general the peaks representing radiation of shifted wave-length appear to be somewhat broader than would be expected from the relative positions, etc., of the secondary radiator and the x-ray rube. Further, some evidence was obtained for weak radiation between the shifted and unshifted peaks. The general or continuous spectrum radiation, also, appears to be somewhat more intense, relative to the line spectra than is the case with the primary radiation. These points have been mentioned by Professor Compton in some of his papers. The relative intensity of the shifted to the unshifted radiation appears to be greater for tungsten than for molybdenum.

With this apparatus we have not observed sharp peaks on the curves that correspond to tertiary radiation, although in certain cases some radiation exists at wave-lengths longer than that represented by equation (1).

The results that we have obtained so far indicate that equation (1) deduced by Professor Compton from his theory of single electron scattering represents the wave-lengths of a large part of the secondary radiation due to primary rays in the K series spectra of molybdenum and tungsten. The molybdenum spectra are in close agreement with the results obtained by Professor Compton and Mr. Woo[3] using an ionization spectrometer with a Soller slit system and small x-ray tube. They also agree substantially with the excellent photographs obtained by Professor Ross[4] with a spectrometer giving very high dispersion and with the photograph and accurate photometer curves published by Dr. Becker.[5] In addition, they show changes in the position of the shifted line (indicated by equation (1) for different values of θ) in the secondary radiation from chemical elements other than carbon, and also a marked diminution in intensity, when the shifted line is drawn out into a band.

[1] NATIONAL RESEARCH FELLOW.

[2] W. Soller, *Phys. Rev.*, **23**, 272 (1924).

[3] A. H. Compton and Y. K. Woo, these PROCEEDINGS, June, 1924, p. 271.

[4] P. A. Ross, these PROCEEDINGS, July, 1923, p. 246; and July, 1924, p. 304.

[5] J. A. Becker, these PROCEEDINGS, August, 1924, p. 342.

AN APPLICATION OF THE QUANTUM THEORY OF BAND SPECTRA TO THE FIRST NEGATIVE DESLANDRES GROUP OF CARBON

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Communicated November 15, 1924

Of the various band systems ascribed to carbon and its compounds, the Deslandres[1] first negative bands are among the most interesting. They lie in the ultra-violet, between the approximate limits $\lambda = 2100 - 2900$ Angstroms, are uniformly degraded toward the red, and present a simple and incomparably beautiful structure. Especial interest attaches to them for several reasons, due indirectly to the fact that ordinary methods of excitation cause the bands to radiate but faintly. Indeed, in the past they have at times been recorded as lines, only the heads being of sufficient intensity to affect a photographic plate. Schniederjost[2] attributed these heads to the so-called "compound line spectrum" of oxygen, since named the "*O-I*" series; and only recently Jevons[3] pointed out this error, giving these "lines" their true classification as the band heads of the first negative group. He arranged these heads in an empirical scheme quite accurately represented by formula, and further extended the list given by Deslandres including some twenty bands in his scheme.

Fowler,[4] in his study of that fascinating spectrum first found in the tails of certain comets, believed that both the first and second negative carbon groups were related to it.

Lemon, by a method of excitation recently developed in this laboratory (and reported separately in these PROCEEDINGS), has been the first to obtain these bands in sufficient intensity for the photography under high dispersion and has made it quite clear that only the first negative group is associated with the "comet tail" spectrum. It was with a view to investigating whether there might be any relationship between the analytical expressions for the two groups of bands on the basis of their quantum theory analysis, that the present work was undertaken, and this paper constitutes a preliminary report of the structure of the first negative system only. Several plates taken in the first and second order of the 21 foot Rowland concave grating serve as a basis of the measurements. The wave-lengths were determined by comparison with two well-known Helium lines in the region studied. ($\lambda = 2945.104, 3187.743$ Å.) By far the greater number of measurements were made on an excellent first order plate, with a dispersion of approximately 2.6 Angstroms per millimeter.

Altogether, twenty of the bands studied were found to fit into the first negative Deslandres' system. The wave-length measurements of the

heads were found to agree quite closely with those given by Deslandres and Schniederjost. Not all of the bands reported by them were found to belong to this system. In particular Deslandres gives two, and Schniederjost five ($\lambda > 2700$ Å) which do not appear on the plates here obtained. On the other hand, two of the bands in the system as herein developed, do not seem to have been noticed by them.

Although the fine structure of the bands is remarkably shown in the photographs studied, it was nevertheless found to be impossible to resolve the lines in the immediate neighborhood of the head. Indeed, on the first order plates, the head is unresolved as far as the ν_0 position. More complete resolution was obtained in the case of two bands, designated later in this paper as $\binom{n'=5}{n=2}$ and $\binom{n'=6}{n=3}$, which were photographed in the second order of the Rowland. Some seven lines closer to the head were measured on this plate, leaving only five lines unresolved.

Owing to this difficulty in resolving the lines in the neighborhood of the head, it was rather difficult to assign the lines properly in accordance with the quantum theory. The structure was first definitely worked out in the case of the two bands before-mentioned, where the resolution near the head could be obtained, and then extended to the other bands by comparison. (It was, of course, possible to do this only on account of the extreme simplicity of the bands, and their similarity of structure.)

In accordance with the present theory, adopting the "half-quantum" interpretation of Kratzer,[5] and the notation of Curtis,[6] we expect, in each band, series of lines, functions of the rotational quantum m, given by:

$$\begin{aligned} P(m) &= \nu = \nu_0 + \tfrac{C_2}{4\pi^2} - (c_0' + c_0)m + c_2 m^2 \quad [(m - \tfrac{1}{2}) \longrightarrow (m + \tfrac{1}{2})] \\ Q(m) &= \nu = \nu_0 + \tfrac{C_2}{4\pi^2} + c_2 m + c_2 m^2 \quad [(m + \tfrac{1}{2}) \longrightarrow (m + \tfrac{1}{2})] \\ R(m) &= \nu = \nu_0 + \tfrac{C_2}{4\pi^2} + (c_0' + c_0)m + c_2 m^2 \quad [(m + \tfrac{1}{2}) \longrightarrow (m - \tfrac{1}{2})] \end{aligned} \tag{1}$$

where ν_0 is the frequency due to electronic and nuclear vibration changes alone: $c_0' = \dfrac{h}{8\pi^2 I'} - \alpha' n'$, $C_0 = \dfrac{h}{8\pi^2 I} - \alpha n$, $C_2 = c_0' - c_0$ I' and I being the moments of inertia of the molecule before and after emission. α_1 and α are constants which depend upon the mutal interaction between rotation and oscillation, while n' and n are the quantum numbers referring to the state of oscillation of the poles of the assumed di-pole molecular model.

By considering the poles of the molecule to act as a non-harmonic oscillator, the theoretical basis of the law which associated the various ν_1 positions of the bands in the system gives in effect:

$$\nu_0 = \nu_e + n'\nu_\rho'(1 - x'n') - n\nu_\rho (1 - xn) \tag{2}$$

where ν_e denotes the frequency due to electronic changes alone, ν_ρ' and ν_ρ the frequency of the oscillator before and after emission, x and x' being small constants associated with the strength of the non-harmonic bond;

while n' and n denote the associated quantum numbers, as before. In this way a doubly infinite series of bands depending upon n' and n is obtained. It should be noticed here that since x' and x are small constants, the coefficients of the quadratic terms of the preceding equation should be small relative to the coefficients of the linear terms, which involve the frequencies ν'_ρ and ν_ρ of the oscillator.

It was found that the series laws (1) were followed to a very close approximation by each of the 18 bands whose structure was studied. In order to

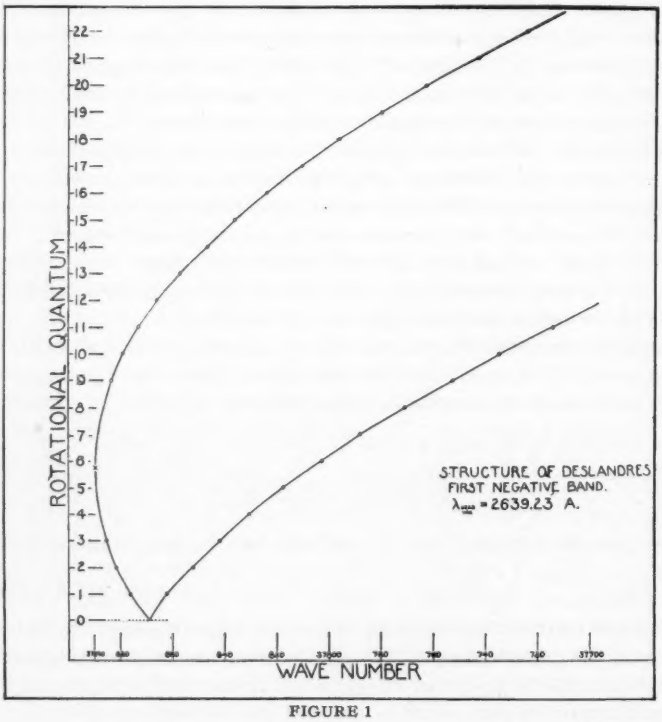

FIGURE 1

obtain the best possible representation for each band, the method of least squares was used to deduce the constants. A simplification of the method of least squares, as developed by Roeser,[7] and applicable to parabolic formulae where the observations of the independent variable are taken at equal intervals, was used. The method is particularly adaptable for use in band spectra computations. Two of the bands, $(\substack{n'=1\\n=1})$ and $(\substack{n'=4\\n=3})$ were quite faint, and it was only possible to measure the positions of the heads.

The ν_0 positions of these bands were inferred approximately by comparing them with their neighbors.

With the exception of a single point mentioned later, the quantum theory outlined above is beautifully confirmed, and indeed by a band system far more extensive than any to which it has been previously applied. For in no case, to the writer's knowledge, has any system of bands been analyzed which compare in simplicity of structure, or in number included, with this group.

Figure 1 shows the fine structure of the band λ 2639.23 Angstroms (vacuum). It is typical of all the bands of the system, the differences of structure of the various members being of a lower order of magnitude. Two general results may be inferred from the fine structure:

Schematic Arrangement of Bands
in
First Negative Deslandres System.
λ^{Head}_{vac} and $\nu_{0\,vac}$.

n' (Initial Oscillation Quantum)

n (Final Oscillation Quantum)	0	1	2	3	4	5	6	7	8
0	2190.28 45637.7	2300.24 43452.8	2420.07 41299.6	2550.97 39179.6					
1		2214.94 45129.3	2325.68 42976.5	2446.48 40855.2	2578.30 38764.8	2722.90 36703.7			
2				2353.08 42477.9	2474.86 40385.5	2607.70 38326.7	2753.49 36297.2		
3					2382.35 41954.7	2505.17 39896.9	2639.23 37869.5	2786.39 35867.0	
4							2537.09 39394.1	2672.79 37397.9	
5									2708.52 36899.5

FIGURE 2

(*a*) Owing to the simplicity of the structure, the radiator of the bands very probably approximates quite closely the dipole molecule on which the theory is based.

(*b*) The absence of a Q-branch is particularly interesting and significant. Such a branch has the significance of holding the rotational momentum constant during change of molecular configuration. On the basis of the Bohr Correspondence Principle[8] it is admissible only when the axis of rotation of the molecule possesses a precessional motion. We are there-

fore led to conclude on this basis that the molecule here in question is in simple rotation about a non-precessing axis perpendicular to the line joining the nucleii.

Figure 2 shows the schematic arrangement of the band ν_0's, assigned in accordance with the initial and final oscillation quantum numbers. The first number gives the wave-length of the head (reduced to vacuum), and the second the wave number of the ν_0 positions as computed from the constants. We expect these to be related in accordance with equation (2). The numerical result which fits very closely the experimental values, is:

$$\nu_0 = 45637.3 + 1701.09n - 25.65n^2 - 2199.12n' + 15.47n'^2$$

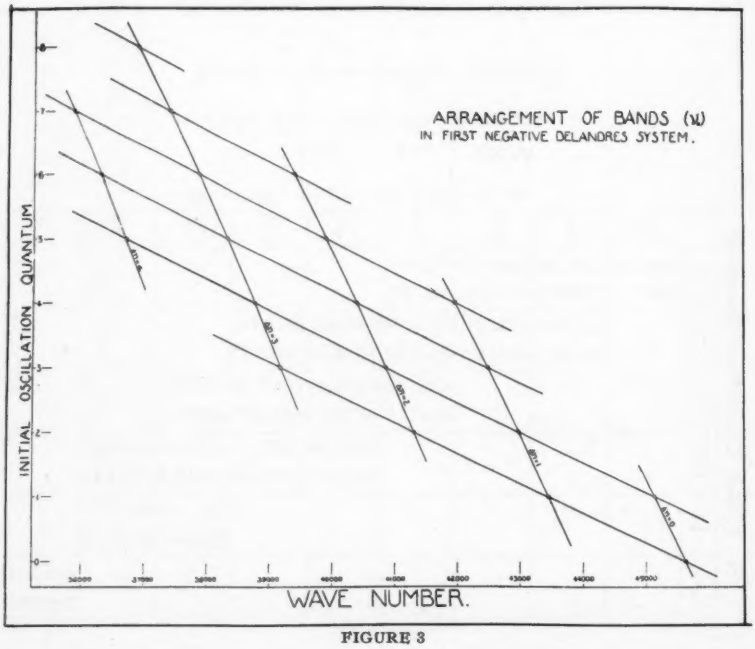

FIGURE 3

We notice here that the prediction of the theory is fulfilled in that the coefficients of the quadratic terms are much smaller than those of the linear terms.

Figure 3 shows graphically the nature of the parabolic regularity, the initial quantum number being plotted against the ν_0 position of the various bands. The one series of parables are plotted according to the condition that

$$n' - n = \Delta n = \text{constant} = 0, 1, 2, 3, 4$$

while the others have each the same value for the final oscillation quantum number, i.e., $n' = 0, 1, 2, 3, 4, 5$.

The accuracy of the parabolic representation far exceeds that with which a graph of this size can be plotted.

Figure 4 exhibits, by means of the same type of schematic representation as in figure 2, the constants of the various bands. This arrangement makes very obvious the approximate linear change of the constants with n and n'. Although quantitatively this linearity is not strictly accurate, it is as close as could be reasonably expected in view of the lack of proper resolution of the heads, and other similar difficulties.

Schematic Arrangement of Band Constants
in
First Negative Deslandres System.
C_0', C_0, and C_2 respectively.

n' (Initial Oscillation Quantum)

n (Final Oscillation Quantum)	0	1	2	3	4	5	6	7	8
0	3.43 4.08 .65	3.25 3.87 .62	3.11 3.70 .59	2.83 3.37 .54					
1		=	3.52 4.20 .68	3.17 3.77 .60	2.93 3.50 .57	2.95 3.47 .52			
2				3.57 4.25 .68	3.44 4.09 .65	3.21 3.82 .61	2.99 3.56 .57		
3					=	3.49 4.14 .65	3.24 3.87 .63	3.14 3.73 .59	
4							3.53 4.20 .67	3.19 3.80 .61	
5									3.59 4.27 .68

FIGURE 4

A peculiar feature of this system, and one which is not in accord with the theory, is that c_0 varies with n', and c_0 with n. This peculiarity has arisen in the study of other band systems which have been reported, but it does not seem to have been the object of much attention. This question will probably be discussed in detail later.

The moments of inertia of the molecule in the vibrationless state ($n' = 0$, $n = 0$) are readily calculated. The value before emission comes out to be 8.07×10^{-40} gm. cm.^{2} while the value after emission is 6.78×10^{-40} gm.cm.^{2} We notice here an extremely large change of the moment of inertia between the initial and final states, amounting to about 16% of the value in the initial state.

A more detailed account of this work will be published upon its completion.

[1] Deslandres, *Comptes Rendus, Paris*, **127** (1903), p. 460, also Kayser's "Handbuch" V, p. 233.

[2] Schniederjost, *Zeit. Wiss. Phot.*, **11** (1904), p. 283, also Kayser's "Handbuch" VI, p. 213.

[3] Jevons, *Phil. Mag., London*, **47**, March, 1924, p. 586.

[4] Fowler, *Mon. Not. Roy. Astron. Soc.*, **70** (1909–10), p. 276, p. 484.

[5] Kratzer, *Sitz. Byer Akad.*, March, 1922, p. 107.

[6] Curtis, *Proc. Roy. Soc. London*, **103A**, May, 1923, p. 315.

[7] Roeser, *Sci. Paper. Bur. Stand.*, Washington, No. 388.

[8] Sommerfeld, *Atomic Structure and Spectral Lines*, English Translation. Methuen, 1923, p. 587.

NEW MEASUREMENTS OF PLANETARY RADIATION AND PLANETARY TEMPERATURES

BY W. W. COBLENTZ AND C. O. LAMPLAND

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For some years the Bureau of Standards has been conducting investigations of the application of instruments and methods of radiometry to various fields of research. One of the most interesting and useful fields appears to be the application of these instruments to certain astronomical problems.

During the past summer further tests of new radiometric instruments were made at the Lowell Observatory, Flagstaff, Arizona. The outstanding results of this investigation are as follows:

By means of a series of transmission screens of water, quartz, glass and fluorite, the radiation emanating from the planets, e.g., Mars, was separated into spectral components and the radiation intensities determined in the spectral regions of 0.3μ to 1.4μ, 1.4μ to 4.1μ, 4.1μ to 8μ, 8μ to 12.5μ, and 12.5μ to 15μ.

In this manner it was possible to determine the shape of the spectral energy curve of that part of the planetary radiation which is transmitted by our atmosphere and thereby form an estimate of the temperature of the effective radiating surface of the planet.

The 640 inch focus of the 40 inch Lowell reflector, which gave an image of the disk of Mars about 2 mm. in diameter, and thermocouples with receivers 0.23 mm. in diameter, were used in these measurements. This combination permitted the isolation of small areas on the planet's disk, and revealed hitherto unobserved and perhaps unexpected temperature conditions.

Radiometric measurements were made on Venus, Mars, Jupiter, Saturn, Uranus, the Moon and on terrestrial sources.

The results obtained verify our observations of 1922 showing that the planetary radiation emanating from Jupiter and from Saturn, and transmitted by our atmosphere, is very small, while the planetary radiation from Venus, Mars and the Moon is, relatively, very intense.

The planet, Venus, is one of the most interesting cases met with in radiometric observations. The surface of the planet is hidden by clouds, and its period of rotation is undetermined. Hence the thermocouple radiometer appears to be a means of obtaining further information on this question. For it was found that not only does the illuminated crescent show the presence of considerable planetary radiation, but the unilluminated part of the disk also emits a large amount of infra-red rays. This raises the question whether the radiation from the dark side of the planet is owing to a rapid rotation, say one to ten days. If the period of rotation is long (225 days) then it seems necessary to assume that the surface of Venus is still quite warm; although the highly selective condition of the planetary radiation at 8 to 12μ may perhaps be interpreted as owing to radiation of the hot gases convected from the illuminated over the dark part of the planetary surface. However, since this involves distances of 800 to 1000 miles over the surface, it seems difficult to reconcile this assumption with the radiative properties of the gases which probably constitute the atmosphere of Venus.

An interesting and important observation is that the intensity of the radiation emitted from near the south cusp in the present position of the planet, Venus—both for the dark and the illuminated regions—is greater than that emanating from corresponding points near the north cusp. This may be owing to differences in the surface conditions as previously observed on Mars. Then, again, it suggests an effect of insolation due to inclination of the axis of rotation, analogous to seasonal changes on Mars and the earth. Further radiometric observations, at different presentations of the planet's surface to the earth, will be required to test this question. If this is seasonal then it should be possible to establish the position of the axis of rotation of Venus.

The measurements on Mars were made on 24 nights and show that the bright regions are cooler than the dark regions; that the sunrise side of the planet is at a lower temperature than the side under the afternoon sun; and that the polar regions are cold—emitting no planetary radiation, and having temperatures down to perhaps —70°C. The temperature of the dark phase on the sunrise side of the planet is very low, probably down to —60°C.

An estimate of the temperature of the irradiated surface of Mars was obtained by two methods, as follows:

(1) By direct comparison of the spectral components of the planetary

radiation from Mars and the Moon, temperatures were obtained ranging from 5°C for the bright regions to 20°C for the dark regions, and

(2) By a comparison of the observed spectral components of the planetary radiation from Mars with similar data calculated from the laws of radiation of a black body, temperatures were obtained ranging from —15°C for the bright regions to 12°C for the dark regions.

The average of all the measurements gives a black body temperature of 8°C as compared with 18°C obtained by direct calibration against the Moon. As a whole, these temperature estimates are in accordance with other observations on Mars. The measurements indicate that the temperature of the brightly illuminated surface of Mars is not unlike that of a cool, bright day on this earth, with temperatures ranging from 5° to 15°C, or 40° to 60°F.

In the case of Venus and Jupiter the planetary radiation seems to be highly selective, and concentrated principally in the spectral component at $8 - 12.5\mu$. As a result, the infra-red temperatures are so inordinately high that this method of analysis seems impracticable in assigning temperatures, though useful in demonstrating selective emission. The water cell transmissions of Jupiter and Saturn indicate very low temperatures —60° to —80°C.

Uranus does not appear to emit planetary radiation, which is in harmony with other astronomical data.

Among the subsidiary investigations were measurements of the radiation from terrestrial sources such as buildings and distant mountain peaks under solar irradiation.

In connection with the theory of radiation exchanges, planetary radiation and planetary temperatures are discussed. It is shown that the symmetrical thermocouple-radiometer, as used in these investigations, always gives a positive response, whatever the temperature of the planet.

THE NUMBER OF FREE ELECTRONS WITH A METAL

BY EDWIN H. HALL

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The question how many "free" electrons there may be within a piece of metal at a given temperature and how this number may vary with the temperature is one of much interest.

If I am not greatly mistaken, some distinguished physicists have entertained the idea that the Boltzmann equation

$$\frac{n}{n_0} = exp\left(-\frac{\phi}{RT}\right) \qquad (1)$$

in which n_0 is the number of atoms and n the number of free electrons per unit volume, holds here, ϕ being the amount of work required to release an electron from an atom within the metal. This seems to me an error, for the application of this equation appears to be limited to cases in which, apart from the influence of ϕ, passage of a particle from state A to state B is neither more nor less difficult than passage in the opposite direction. Such cases are, for example, those in which A and B are different gaseous conditions or different solution conditions of the particles.

According to my view of the matter, the relations which exist between the atoms, the free electrons and the positive ions, within a metal are essentially those of dissociation equilibrium. It is well known that for such a case, if one parent particle yields two product particles, we have, as the equilibrium constant at any given temperature.

$$K = \frac{n^2}{n_0}, \qquad (2)$$

where n_0 is the number of undissociated and n is the number of dissociated particles per unit volume. This equation, which is a case under the *mass law*, can be derived from mere probability considerations touching kinetic conditions, and it holds, I believe, as well for the interior of a metal as for a gaseous or solution state.

Now it is a familiar fact that the value of K in any case of dissociation equilibrium depends on the ratio of two velocities, or facilities, one being that of the dissociation process, the other that of the re-association process, and the two main laws of thermodynamics tell us nothing about this ratio. By means of the so-called third law, however, considerable success has been attained in efforts to calculate values of K, in certain cases, from thermal data. If ionization within a solid metal were thus subject to the application of the third law, I should probably be uncomfortably hampered in the assumptions I could make regarding the value of K at any temperature and its rate of change with temperature; but I shall now undertake to show that the applicability of the third law in this case is not proven.

The third law is in fact merely a certain relation between the A and the U of the Helmholtz "free-energy" equation,

$$A - U \text{ (or } \phi) = T\frac{dA}{dT}, \qquad (3)$$

But so far as my observation goes, whenever this law is used to calculate the value of a K, an expression for A in terms of K is introduced which is or can be obtained by means of the van't Hoff reaction chamber argument. Now this argument assumes the possibility of forcing the original material of the reaction isothermally and reversibly into the reaction space and taking the products of the dissociation, separately, by isothermal re-

versible processes, out from this space, the items of necessary work involved in the whole operation being either negligibly small or calculable by the laws of perfect gases. It is not clear to me that the process or state of ionization within a metal can be successfully dealt with in this way. Even if a "semipermeable membrane" for straining the ions out of the metal could be found, the non-reversible work of the straining process probably could not be reduced to a negligible quantity by making the operation a slow one. There is, I think, an essential mechanical difference between the condition of the ions within a solid metal and that of ions in a liquid solution.

The special purpose of this paper is to defend certain assumptions which I make in framing a theory of electric conduction in metals—namely, that the number of free electrons may in some metals be as great as 2 or 3 per cent of the number of atoms, at ordinary temperatures, and that the number of free electrons increases with rise of temperature at a rate of which need not be in accord with the so-called *reaction isochore* equation,

$$\phi = RT \frac{d \ln K}{dT} \tag{4}$$

According to my speculations, applied to such data as I have, the "ionizing potential" in the many metals I have studied varies from about one-eighth volt in cobalt to about one-third volt in iron, at 0°C—a much smaller quantity in each case than the ionizing potential of the corresponding metal vapor.

RECENT MEASUREMENTS OF THE JOULE EFFECT FOR CO_2

By Frederick G. Keyes and Francis W. Sears

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Read before the Academy November 10, 1924

The net energy change obtainable when a fluid changes volume by passing from a compressed condition in one vessel to another exhausted vessel is a quantity of very fundamental importance in promoting an understanding of the attractive forces which exist between molecules.[1]

It may be observed that the origin of the energy delivered when a gas expands without doing mechanical work lies in the work done against the mutual attractive forces of the molecules and also in a possible change of molecular species. The sign of the energy obtainable from either source is the same. Consequently, particular care is required in planning the

measurements in order that the one effect may be separated from the other.

The possibility of separating the effects depends primarily either on an assumed knowledge of the dependence of attractive effect on volume and possibly on temperature or the dependence of the molecular dissociation on temperature and pressure.[2] The latter functional form is well known as far as it relates to perfect gases and is sufficiently accurate to give the heat effect of a shift in molecular species provided the Joule effect measurements are favorably chosen.

Our quantitative knowledge concerning the attractive forces effective between the molecules of a gas is almost nil. It is true that the van der Waals' and other equations of state are based on considerations which lead to functional forms intended to represent the effect of the attractive forces, but these equations differ widely. For example, the van der Waals' equation is based on the assumption that the resultant force of attraction is a volume function only, independent of the temperature, whereas the Clausius equation requires that the force of attraction be a function of both the volume and temperature. Neither equation, as is well known, is in good accord with the existing body of experimental data of various kinds. It is therefore clear that much insight is to be gained into the fundamental characteristics of the attractive forces existing between molecules if accurate measurements of the Joule effect can be executed.

From the thermodynamic point of view, the expansion of an isolated gas without development of mechanical energy may be represented by the equation $du = O$ where du is the total change of internal energy in the fluid. In terms of the temperature T and the volume v, the internal energy of the expanding gas may be written down:

$$du = \left(\frac{\delta u}{\delta T}\right)_v dt + \left(\frac{\delta u}{\delta v}\right)_T dv \ldots\ldots\ldots \quad (1)$$

In this latter equation it is convenient to represent $(\delta u/\delta T)_v$ by the symbol C_v, the specific heat capacity at constant volume. By means of the second law of thermodynamics $(\delta u/\delta v)_T$ may be replaced by $T(\delta p/\delta T)_v - p$ and there results:

$$du = O = C_v\, dt + \left(T\left(\frac{\delta p}{\delta T}\right)_v - p\right) dv \ldots\ldots\ldots \quad (2)$$

The final result of Joule's experiments showed that there was an in appreciable net change of energy when air at 22 atm. expanded from one vessel into a similar exhausted vessel. The gas-filled container of course cooled and the exhausted vessel warmed, but the temperature of the system as a whole showed no measureable change. It can now be estimated that the change in temperature in Joule's original experiment was less than 0.001°.

The pressure volume and temperature data of CO_2, the gas used in these measurements, have been shown to be accurately represented between 0° and 100° by an equation of state[3] of the following form where α, β, A and 1 are constants:

$$p = \frac{RT}{v-\beta e^{-\alpha/v}} - \frac{A}{(v+1)^2} \cdots\cdots\cdots \quad (3)$$

If the associated fraction of doubled molecules is $y = Ce^{2\Delta H/RT} R/v$ and small, for a not too high pressure (3) may be written:

$$p = \frac{R(1-y/2)T}{v-\beta e^{-\alpha/v}} - \frac{A}{(v+1)^2} \cdots\cdots\cdots \quad (4)$$

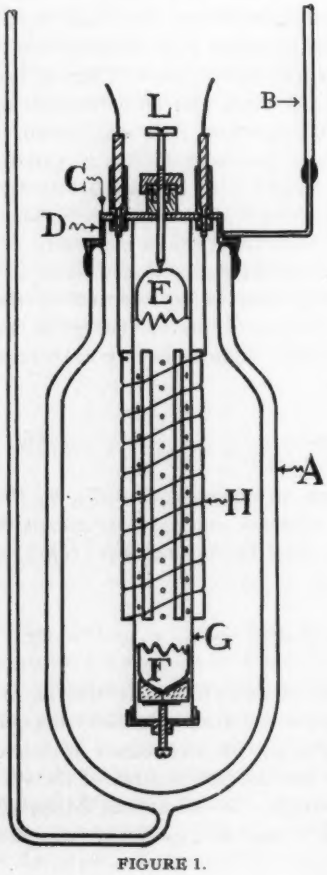

FIGURE 1.

The second term of the right hand member of equation 2 may be found from the partially generalized equation of state (4) and (2) becomes on integrating:

$$O = C_v(T_2-T_1)+A\left[\frac{1}{v_1+1}-\frac{1}{v_2+1}\right]+ [y_1 - y_2]\Delta H \cdots\cdots \quad (5)$$

The subscripts one and two refer to the conditions of the experimental system before and after the measurement, and ΔH is the heat of dissociation per unit quantity of the gas.[4]

The apparatus employed is represented in Figure 1. A is a two liter flask whose inner member is of small weight. G represents a thin walled steel tube fastened to the steel cover C which latter was ground to the steel rim cemented to the flask. The tube G was perforated with about 0.5 mm. holes giving a surface of approximately 7 cm.^{2} Lateral vanes secured to this tube support the platinum wire whose resistance change was used as a measure of the temperature. The drop in temperature in the first two runs in table I was measured with a ten junction copper constan thermocouple instead of the platinum wire shown. The glass

bomb *EF*, enclosed in the perforated steel tube, was formed with a slight depression at the upper end. Utilizing the pressure exerted by the screw actuated part *L*, the glass tube may be exploded releasing the contained gas immediately. The flask *A* is obviously pumped out through *B* before releasing the gas.

The temperature changes obtained for expanding CO_2 are given in the following table.

TABLE I

JOULE EXPERIMENTS SHOWING THE DROP IN TEMPERATURE WHEN CO_2 EXPANDS AT 30°

PRESSURE IN ATM. IN EXPLODABLE BOMB	ΔT OBS.	ΔT CAL. EQ. 5
16.5	0.17°C	0.12°C
13.3	0.08	0.07
15.6	0.06	0.09

It will be noticed that the temperature changes observed are of the order of magnitude of those expected. The results are, however, tentative and an all-metal apparatus of small heat capacity is being designed, which will enable temperature changes of the order of one degree to be obtained. Moreover, it is necessary to carry out measurements over as long a range of temperatures as possible and a compact metal Joule calorimeter is preferable for this purpose to the improvised calorimeter described in this paper.

[1] J. P. Joule, *Phil. Mag.*, **23**, 1845. The name "Joule Effect" here given to the net energy change appearing in a fluid after expansion into a vacuum is perhaps misleading since Gay-Lussac had made an analogous experiment reported upon in 1907. Preston's "*Theory of Heat*," page 286, 1904 edition uses the designation "Joule experiment."

[2] There is neglected here any energy changes which would occur due to a shift with pressure in the amount of adsorbed fluid or the heat effect of adsorption when the expanding gas enters the exhausted vessel.

[3] F. G. Keyes, *Proc. Nat. Acad. Sci.*, **3**, 323 (1917); H. B. Phillips, *J. Math. Phy., M. I. T.*, **1**, 1 (1921).

[4] The data for the association may be taken from a recent paper dealing with the Joule-Thomson effect. F. G. Keyes, *J. Amer. Chem. Soc.*, **46**, 1584 (1924).

THE COMET TAIL SPECTRUM AND DESLANDRES' FIRST NEGATIVE GROUP

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Communicated November 15, 1924

Fowler[1] has shown that the bands occurring in the tails of certain comets, notably Daniels (d 1907) and Morehouse (c 1908) can be reproduced in the laboratory under low pressures (0.01 mm.) of carbon compounds, and his experiments seem to indicate the monoxide as the origin. He further

states that conditions developing them bring out, also, "the two negative series of bands in the ultra-violet described by Deslandres."

Merton and Johnson have developed more recently[2] the comet tail spectrum in 20 mm. of helium with very small partial pressure of a residual carbon compound which they believe, in agreement with Fowler, to be CO.

Neither of the above authors appear to have produced this spectrum with intensity sufficient to allow of its photography under high dispersion.

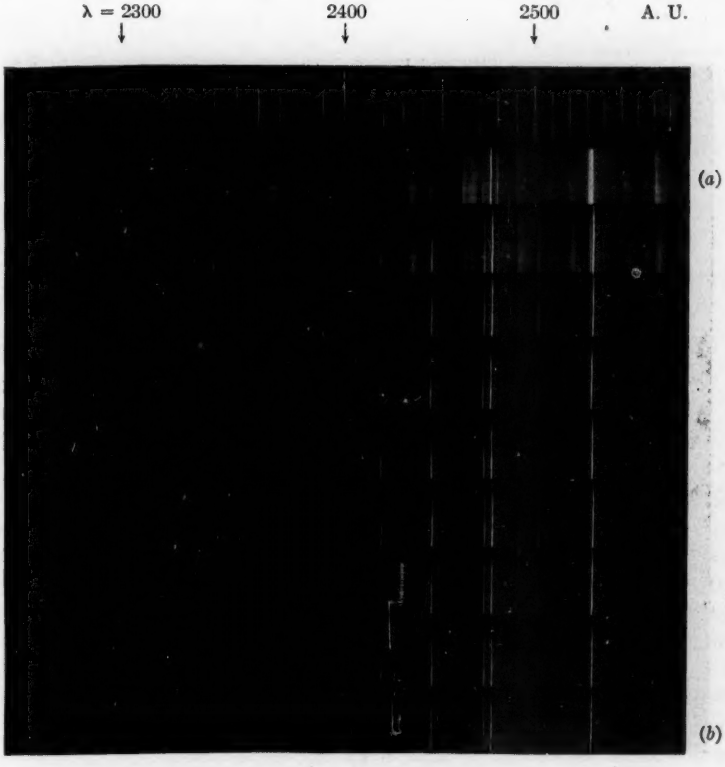
It has been found that a long vacuum tube of the Wood type having 0.4 cm. bore when filled with 2 cm. of helium pumped by circulation through activated carbon[3] will furnish an extremely brilliant comet tail spectrum provided the partial pressure of carbon compounds is of the order of 10^{-4} mm. Unfortunately, the composition of the residual carbon compounds so obtained is quantitatively unknown, but CO_2 and various hydro-carbons are present. Further experimental work is in progress on this point.

That there is a definite connection between the comet tail spectrum and the *first* negative Deslandres group is clearly shown on quartz spectrograph plates reproduced in the two photographs. By varying current density through the tube, the two different sets of bands are either almost completely isolated from all other spectra, or else entirely suppressed. In all cases their relative intensities are qualitatively the same, and certain indications, also from analysis of their structure, suggest that they may originate from the same source. No indication of any connection between the second negative Deslandres group and the comet tail spectrum has appeared in the course of this work.

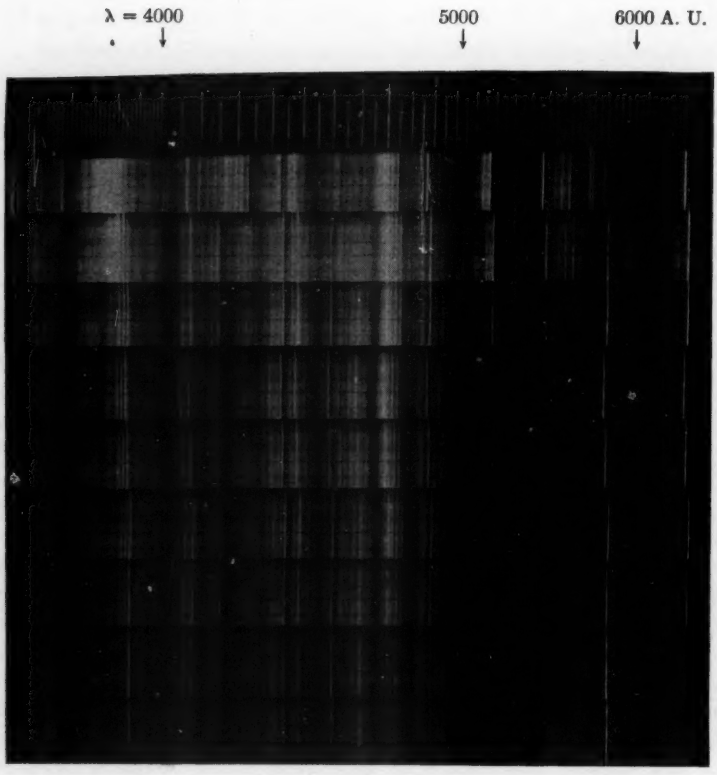
The brilliance of the spectra produced is so great as to make it possible for them to be photographed in the first order of a 21-foot Rowland concave grating, and a discussion of their structure from the point of view of the quantum theory of band spectra has been carried out by Mr. C. M. Blackburn, and is published separately in these PROCEEDINGS.

It is worthy of note that heating the tube with a flame, or by means of the current itself, suffices to change its color from pink to blue, and to cause the suppression of the comet tails and first negative group, and the development of the triplet system (referred to by Merton and Johnson) and the Ångstrom bands. Normally, the change is reversible as the tube is cooled, but on two occasions the development of the triplet system has been permanent and accompanied by the complete extinction of the spectrum of Helium, and a marked reduction of gas pressure inside as exhibited by the length of the dark space. Conditions hardly permit of the hypotheses of occlusion in the ordinary sense of diffusion of the Helium through the tube, and one is reminded of some early work of Berthelot[4] on the apparent disappearance of Helium when associated with carbon compounds.

The comet tail spectrum has been obtained also in discharge tubes of the



The first negative Deslandres group.
(*a*) High current density
(*b*) Low current density



The comet-tail bands.

(*a*) High current density.
(*b*) Low current density.

type used in producing the continuous spectrum of hydrogen[5] having a hot cathode when evacuation is very high and only the residual gases left above previously evacuated carbon cooled to liquid air temperatures are present. Such luminosity, however, is too feeble to betray the Deslandres' bands, if present.

This confirms the opinion that Helium plays only a secondary rôle in the excitation of these spectra, but nevertheless a necessary one for their production with great intensity.

[1] *Mon. Not. Royal Astron. Soc.*, **70**, Dec., 1909, p. 176., April, 1910, p. 484.

[2] *Proc. Roy. Soc., London*, **103A**, June, 1923, p. 383.

[3] Lemon, *Physic Rev.* (2nd Ser.), **9**, April, 1917, p. 336; **14**, Oct., 1919, p. 281; Lemon and Blodgett, *Ibid.*, Nov., 1919, p. 394.

[4] Berthelot, *Am. Chem. Phys.* (VII), **11**, 1897, p. 19.

[5] Lemon, *Nature*, **113**, Jan., 1924, p. 127.

THE PERIODIC STRUCTURAL REGULARITIES IN SPECTRA AS RELATED TO THE PERIODIC LAW OF THE CHEMICAL ELEMENTS

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BUREAU OF STANDARDS, WASHINGTON

Read before the Academy November 10, 1924

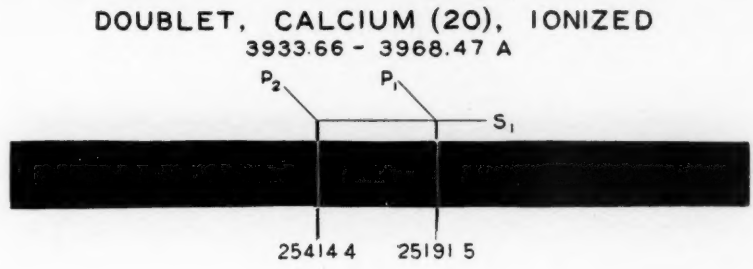
The periodic law of the chemical elements, first established in 1870 on the basis of atomic weights, chemical valencies, and atomic volumes, was later supported by the discovery that other properties (compressibilities, expansion coefficients, etc.) exhibited similar periodicities in their dependence on atomic weights, or rather on the corresponding atomic numbers. It was natural to assume that the structures of the optical spectra, in the production of which the main rôle is probably played by the same outer electrons as are involved in the chemical combinations of the atoms, should also exhibit analogous periodicities through groups of elements. About thirty years ago, when the structures of some of the simpler spectra were first discovered, it appeared that the emission of doublets by elements of odd valency, and triplets by those of even valency might be a general rule (Rydberg's law). The disclosure of doublets in the spectra of alkaline earths appeared, however, to violate this rule, but in 1914 these systems were recognized as belonging to ionized atoms so that a relation between the line structure of a spectrum and the position of an element in the periodic table was reëstablished. This relation was clearly expressed in 1919 by the *displacement law* of Kossel and Sommerfeld, and the extension of Rydberg's *alternation law*.

The *displacement law* states that the spark spectrum (radiation from the ionized atoms) of any element, resembles in structure the arc spectrum (radiation from the neutral atoms) of the preceding element. The modern *alternation law* applies to both arc and spark spectra; it states that even and odd structures characterize the arc spectra of alternate chemical elements which occupy columns I to VIII of the periodic system, while conversely odd and even structures characterize the first spark spectra of the same elements. The experimental verification of these laws has come only recently with the discovery of regularities in the complex spectra which characterize many of the chemical elements.

In general, spectral lines may be either simple (e.g., red radiation from cadmium), or they may occur in groups (e.g., two yellow lines of sodium), and in both cases related lines or groups of lines may be expressed by a mathematical formula representing a so-called spectral series. Such series have been discovered in the spectra of about 30 of the chemical elements, for the most part in the relatively simple spectra. Elements like titanium, vanadium, chromium, and those of the iron and platinum groups, being characterized by very complex spectra, have resisted practically all attempts to arrange the lines in regular sequences, but in many of these cases significant groups have recently been detected, and interpreted according to a comprehensive but relatively simple plan of spectral structures.

Every spectral line (radiation frequency) is thought to originate with a definite transition between two energy states of an atom, each state being defined by a set of quantum numbers. The characteristic groups of lines, now generally called multiplets, thus arise from transitions between energy states which are in reality not simple; the initial, the final, or both states may be multiple valued. In the case of the alkalis (column I of the periodic system), the normal state (zero radiant energy) of the neutral atoms is represented by a single value; all energized states are double so that the doublet structures in the arc spectra of these elements are thereby explained. The arc spectra of the alkaline earths (column II of the periodic system), consist of series of singlet and series of triplet lines—doublets are absent. The normal state is again represented by a single term but different energized states may be either single or three fold. For the remaining columns of the periodic arrangements the energized states of the atoms may be even more complex, and the possible transitions give rise in some cases to groups consisting of fifteen, or more, related spectral lines.

Two systems of terms, singlet and triplet, have been indicated for the spectrum of neutral calcium. In the arc spectrum (from the neutral atoms) of scandium, which follows calcium, doublet and quartet systems have been recognized, while the arc spectrum of the next succeeding element, titanium, has been found to come from singlet, triplet and quintet systems of terms. Each system of terms, contains a succession of types differing



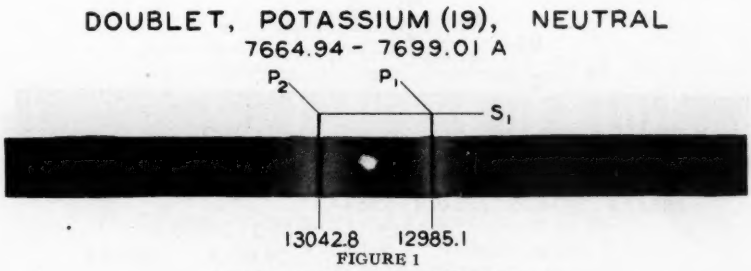
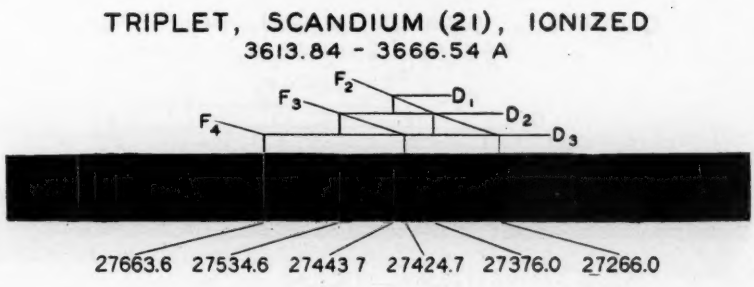


FIGURE 1

Doublets in the spectra of K and Ca+.



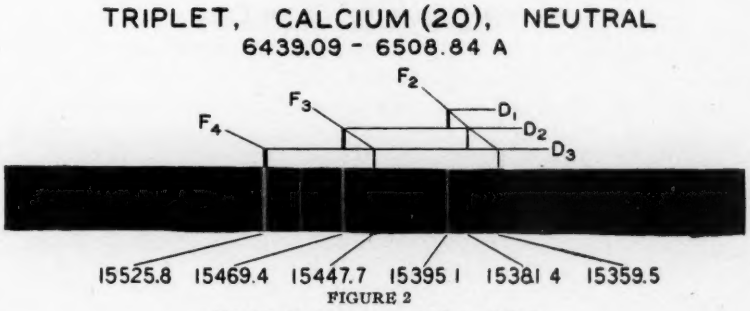


FIGURE 2

Triplets in the spectra of Ca and Sc+.

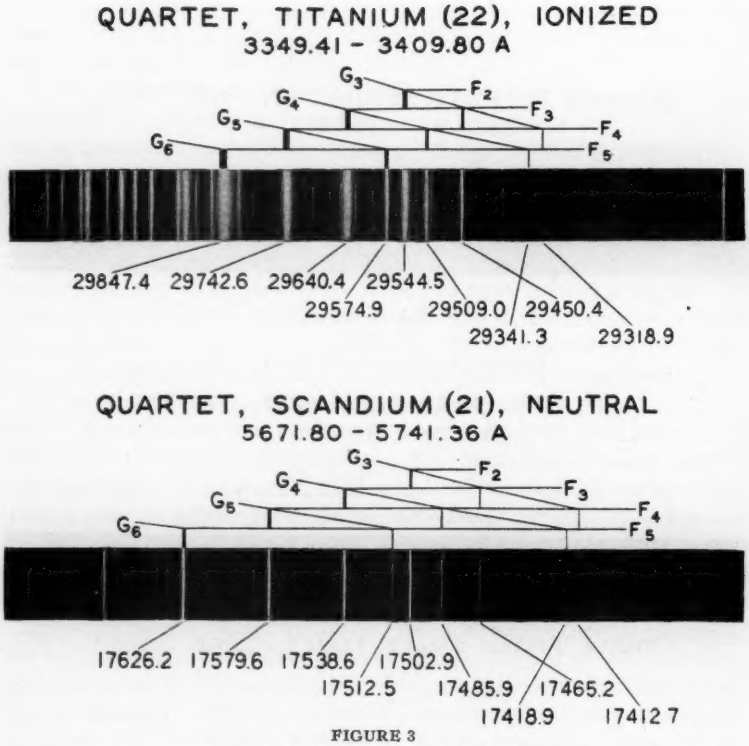
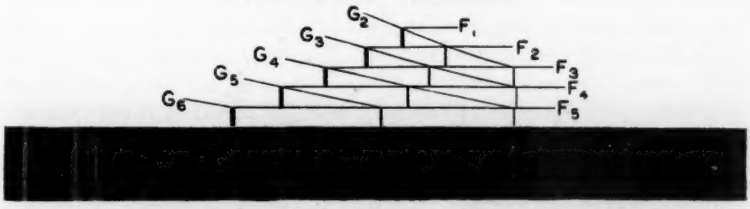


FIGURE 3

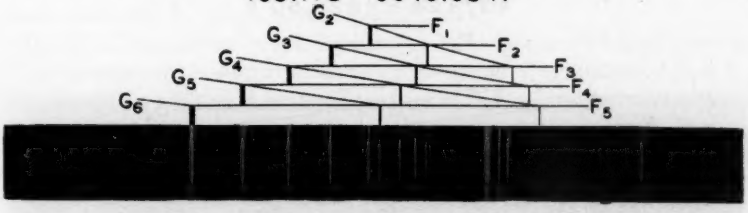
Quartets in the spectra of Sc and Ti+.

QUINTET, VANADIUM (23), IONIZED
3093.10 - 3145.98 A



32320.6	32224.8	32137 7	32058.6	31987.8
	32030.3	31978.3	31936.9	31905.7
		31783.9	31783 7	31777.4

QUINTET, TITANIUM (22), NEUTRAL
4981.73 - 5040.63 A



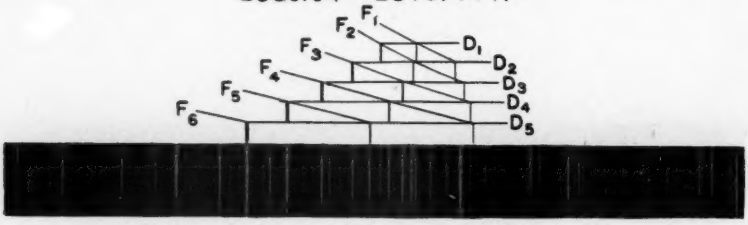
20067.7	20030.2	19996.4	19965.7	19937.5
	19930.0	19914.7	19903.4	19895.6
		19814.4	19821.6	19833.3

FIGURE 4

Quintets in the spectra of Ti and V+.

SEXTET, CHROMIUM (24), IONIZED

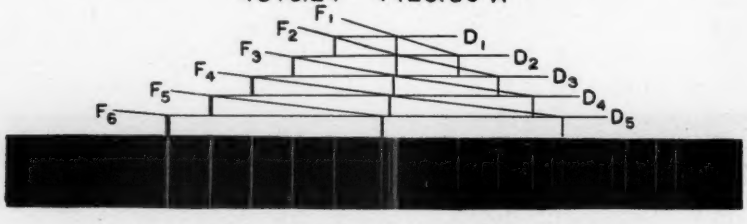
2835.64 - 2878.44 A



35255.1	35160.9	35079 4	35007.8	34943.4	
	34968.1	34923.2	34892 4	34872.5	34861.7
		34730.9	34736.5	34757.3	34790.8

SEXTET, VANADIUM (23), NEUTRAL

4379.24 - 4429.80 A



22828.6	22800.0	22772.7	22745.5	22717.9	
	22686.6	22681.4	22678.6	22677.0	22677.0
		22568.1	22587.4	22610.0	22636.1

FIGURE 5

Sextets in the spectra of V and Cr+.

by one unit of azimuthal quantum number and designated as S, P, D, F, G, etc., in the order of increasing integers. The multiplicities, except for the singlet system, increase with progression in type until a maximum and permanent value which defines the system, is attained. These multiplicities of the energy states as represented by the polyfold spectral terms seem to depend on the number of outer electrons of the atoms. For in the case of an equal number of outer electrons the multiplicities are the same, being even for an odd number of outer electrons and odd for an even number of outer electrons. This expresses the *alternation law* for arc spectra. When an atom is *ionized*, one outer electron is removed, so that the atomic number is, in effect, reduced by this one unit and, hence, the spectral structures for ionized atoms are changed to systems of odd multiplicity if the spectrum of the neutral atoms shows even multiplicity, and vice versa. This expresses the *displacement law* of arc and spark spectra.

These laws are illustrated in Figures 1 to 5, each of which shows typical multiplet structures in the arc and spark spectra of adjacent elements in a portion of the 4th period. The wave-length range of each spectrum is given above the spectrum, and the vacuum wave-numbers of the individual lines are below. The interpretation of each group is contained in the corresponding diagram in which horizontal lines represent the low energy level, oblique lines the higher excited states, the sub-levels of the different types of combining terms being distinguished by inner-quantum-number subscripts. Intersections of these lines represent possible combinations of terms giving rise to the emission of spectral lines.

In table I, the systems of regularities now known for arc and spark spectra of ten elements in the fourth period are represented, the numbers, 1, 2, 3, 4, etc., indicating the maximum multiplicities in the spectral terms or atomic energy levels.

The structures for spectra of atoms in the fifth period of elements are not so completely analyzed, but insofar as they are known or may be predicted they are represented in table II.

The periodicity of structural regularities in spectra as related to the periodic law of the chemical elements is thus revealed in the verification of the displacement and alternation laws. Practically all the structures here referred to are in beautiful accord with the quantum theory of spectral line emission as developed by Bohr, Sommerfeld, Landé and others. During the past three years more than 5000 spectral lines have been classified by Catalán, Gieseler, Kiess, Laporte, Meggers, Russell and Walters. With the further development of methods of attack, it seems probable that practically all complex spectra will be fully interpreted in a period of time not greater than that already expended in the classification of simpler spectra—especially if additional workers can be brought into this fascinating field.

The information as to atomic structures and energies derived from the identification of spectral regularities has already given many clues to the interpretation of astrophysical phenomena as well as to the explanation of empirical facts connected with practical applications of the spectroscope in the laboratory. It has, for example, given a physical basis to spectrochemical analysis by showing which lines may be expected to be most sensitive in spectrographically revealing the presence of minute traces of any chemical element. In arc spectra, these *raies ultimes* are produced by the return to normalcy of those atoms which have been energized the minimum amount consistent with a direct return to the normal state, and the loss of one unit of azimuthal quantum. The *raies ultimes* in spark spectra are, in general, different from those in the arc because the corresponding energized states are different, but the rule that the most sensitive lines arise from the minimum possible decrease in energy coincident with a unit reduction of azimuthal quantum when the atoms, whether neutral or ionized, return to their normal states appears to be true in all cases.

TABLE I

SYSTEMS OF SPECTRAL STRUCTURES FOR TEN ELEMENTS OF THE FOURTH PERIOD

(*a*) Arc Spectra, Neutral Atoms

COLUMN	I	II	III	IV	V	VI	VII	VIII		
Element	K-19	Ca-20	Sc-21	Ti-22	V-23	Cr-24	Mn-25	Fe-26	Co-27	Ni-28
Systems		1		1						(1)
	2		2		2				2	
		3		3		3		3		(3)
			4		4		4		4	
				5		5		5		(5)
					6		6		6	
						7		7		
							8			

(*b*) Spark Spectra, Ionized Atoms

COLUMN	I	II	III	IV	V	VI	VII	VIII		
Element	K-19	Ca-20	Sc-21	Ti-22	V-23	Cr-24	Mn-25	Fe-26	Co-27	Ni-29
Systems	?		1		1?				(1)	
		2		2		2?		2?		(2)
			3		3		3?		(3)	
				4		4		4		(4)
					5		5		(5)	
						6		6		
							7			

The numbers 1, 2, 3, 4, etc., represent the maximum multiplicities in the spectral terms or atomic energy levels belonging to the corresponding systems of spectral structures, singlets, doublets, triplets, quartets, etc. Those in parentheses, still unknown, are suggested from considerations of symmetry.

TABLE II

SYSTEMS OF SPECTRAL STRUCTURES FOR TEN ELEMENTS OF THE FIFTH PERIOD

(*a*) Arc Spectra, Neutral Atoms

COLUMN	I	II	III	IV	V	VI	VII	VIII		
Element	Rb-37	Sr-38	Y-39	Zr-40	Cb-41	Mo-42	?-43	Ru-44	Rh-45	Pd-46
Systems		1		1?						(1)
	2		2		2?				(2)	
		3		3		3?		(3)		(3)
			4		4		(4)		(4)	
				5		5		(5)		(5)
					6		(6)		(6)	
						7		(7)		
							(8)			

(*b*) Spark Spectra, Ionized Atoms

COLUMN	I	II	III	IV	V	VI	VII	VIII		
Element	Rb-37	Sr-38	Y-39	Zr-40	Cb-41	Mo-42	?-43	Ru-44	Rh-45	Pd-46
Systems	?		1		(1)				(1)	
		2		2		(2)		(2)		(2)
			3		(3)		(3)		(3)	
				4		(4)		(4)		(4)
					(5)		(5)		(5)	
						(6)		(6)		
							(7)			

The numbers 1, 2, 3, 4, etc., represent the maximum multiplicities in the spectral terms or atomic energy levels belonging to the corresponding systems of spectral structures, singlets, doublets, triplets, quartets, etc. Those in parentheses, still unknown, are suggested from considerations of symmetry.

NOTES ON NEODYMIUM OXIDE

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Communicated December 1, 1924

Spectrum of the Glowing Oxide.—Neodymium oxide is one of the very few solids with a discontinuous spectrum. The spectrum which was known long before neodymium was separated from its fellow element praesodymium, was briefly described by Bunsen[1] in 1864, who in the same communication mentions the discovery by Bahr[2] of the similarly banded spectrum of erbium oxide. Thus far, however, no thorough-going study seems to have been made of this class of spectrum.

Viewed through a spectroscope of small dispersion the spectrum of the glowing oxide shows six easily distinguishable bands, provided that the

temperature does not greatly exceed 1000°C. At higher stages of incandescence the bands merge and the spectrum cannot be distinguished from that of a black body of like temperature.[3]

With the spectrophotometer a somewhat more complete resolution is obtained (see fig. 1). Ten or more crests upon the brightness curve of the visible spectrum are then discernible and these are doubtless merely envelopes of groups in a much more complicated but almost wholly submerged structure. Those brought out in a recent measurement fall into two sets, such that the frequency differences between neighbors in a given set are multiples of a numerical constant which is the same for both sets. This constant is 18.5 which is the Tanaka interval[4] for neodymium so that there would seem to be a relation between the spacing of the bands in the spectrum of glowing neodymium oxide and of those in the spectrum of cathode luminescent substances in which neodymium is the activating element. Having ascertained by inspection that such a relation holds at least approximately the matter was tested by constructing a scale of the interval in question and slipping it along until it matched the crests—as shown in figure 1. The dotted vertical lines crossing the crests have been drawn thus and it will be seen that they correspond to the maxima, marked A, quite as closely as the data will permit these to be found. By shifting the scale slightly the second set marked B has been similarly located.

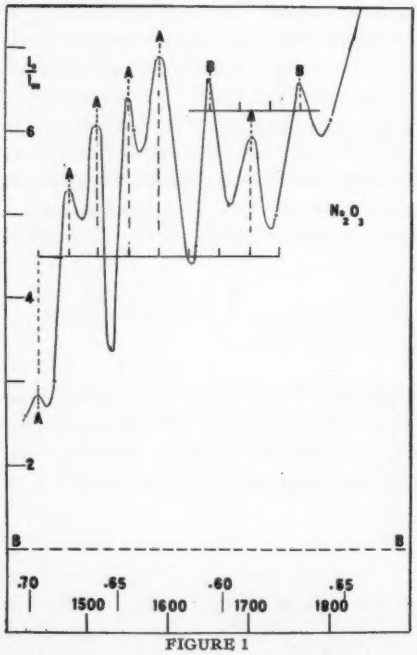

FIGURE 1

Emission bands in the spectrum of glowing neodymium oxide.

In this way the wave-lengths in table I have been derived from the spectrophotometric data indicated graphically in figure 1 where the curve of the ratio of intensity (I_o) of the glowing neodymium oxide to the brightness (I_{BB}) of the corresponding region in the spectrum of a black body at the same temperature is plotted for the longer wave-lengths of the visible spec-

trum (0.700μ to 0.550μ). The curve rises to ever higher values towards the violet; the ratio being 42 at the wave-length 0.4675μ.

Evidences of Luminescence.—To get the banded spectrum at its best and to bring out the other effects described in these notes the oxide must be heated by direct contact with a hydrogen flame following the procedure established in previous studies of luminescence at high temperatures. It was under such conditions that the measurements depicted in figure 1 were made.

It will be noted that the brightness of the neodymium oxide at the temperature of the experiment (about 900°) is greatly in excess of that of the black body with which it was compared. At the above temperature therefore there is luminescence of the oxide superimposed upon the incandescence, a condition suggested by the spectral structure described in the preceding paragraph. Above 1000°C the banded spectrum disappears as already noted. It is at the lowest stages of incandescence that the relative excess of brightness above that of a black body attains its maximum. This is a property common to other luminescent oxides but in most cases the effect is confined to the shorter wave-lengths.[5] In neodymium oxide the glow extends throughout the brighter regions of the spectrum and it has been found possible for the first time in the course of these investigations to carry measurements down to temperatures below that at which the maximum of luminescence occurs. At these lowest temperatures the incandescence of the black body with which we wish to compare the brightness of the neodymium oxide is too dim for easy measurement with the optical pyrometer and recourse is had to extrapolations based upon the following procedure.

If the hydrogen flame, the axis of which is parallel to the glowing surface be moved away stepwise the temperature of the surface is found to be in linear relation to the distance from the axis of the flame. By a slight extension of this straight line temperatures from 700° down to 600° are estimated.

The curves in figure 2 depicts the changes in the ratio of I_o to I_{BB} when the temperature is varied from 600°C to 1000°C. From the lower temperature the ratio rises to its maximum value of over 800, at about 700°; then falls, rapidly at first, approaching unity shortly above 1000°. The graph

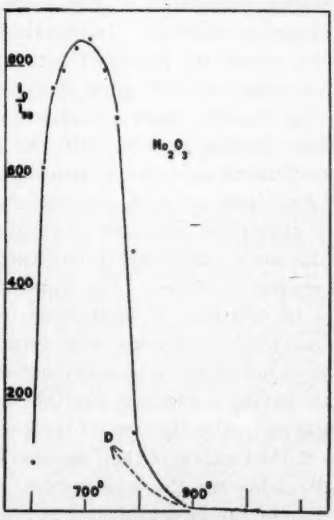

FIGURE 2
Luminescence of neodymium oxide at lower stages of incandescence.

applies to the group of bands in the red end of the spectrum but similar although not strictly identical results are obtained for the shorter wavelengths.

Fatigue: A Further Characteristic of Luminescence.—Neodymium oxide when heated in the hydrogen flame shows fatigue of two kinds. (1) When heated beyond the range of temperatures indicated in figure 2—say to 1200°C—and allowed to cool, it returns along a lower path indicated by the dotted line *D*, the position of which is determined by the duration and temperature of the previous heat treatment. (2) When maintained at any temperature at which luminescence occurs there is a falling off of brightness with the time. This second type of fatigue likewise associates Nd_2O_3 with all or nearly all other known luminescent bodies.

Bulk and Bead Spectra.—When a bead of microcosmic salt containing neodymium oxide is brought to incandescence the emission spectrum differs markedly from that observed when the glowing oxide is in bulk instead of being in dilute suspension or possibly in solution in the molten sodium phosphate. This *bead spectrum*, as we may term it, is of interest because of its bearing upon the relation between the absorption spectrum and the emission spectrum of neodymium. An observer comparing the emission spectrum of such a bead with the absorption spectrum of the same bead when incandescent but transmitting light from behind would find the two spectra identical as did Bunson in the experiments cited in the opening paragraph of this communication; the one spectrum being a reversal of the other. Indeed the best way of locating emission bands in the blue, which are discerned with difficulty, is to reverse them, whereupon they stand out with great sharpness.

On the other hand a comparison of the emission spectrum of neodymium oxide glowing in bulk with the absorption spectrum of a solution of a neodymium salt shows more apparent discrepancies than resemblances. It may, however, be shown that the bead spectra (emission and absorption), the absorption spectrum of solutions, and the *bulk spectrum* of the glowing oxide (as we may term it to distinguish it from the bead spectrum), all have the same structure. The numerous determinations of the banded spectra of solutions of neodymium and the associated elements have been scrutinized by Kayser with great discrimination. If we take his list of bands belonging to neodymium[6] we find that they too may be arranged in sets having a common constant frequency difference of 18.5 (the Tanaka interval); also that two of these sets correspond to sets *A* and *B* of table I as to the location of their members and that the bands of the bead spectrum fall readily into the same system. It will be understood of course that these relations can be established at present only to the degree of precision with which the locations of more or less vague and often overlapping bands are known; that is to say for the most part to 0.001μ. It is clear, however,

that the various spectra of neodymium are all parts of a single structure.

The relationship may be stated as follows:

(1) There are two banded emission spectra, the "bulk" spectrum and the "bead" spectrum (table I). Although there appear to be only two coincidences (at 1589 and 1651) each of the two spectra may be arranged in two sets A and B as shown in the table, and *these two sets are identical* although different places are in general occupied by the bands of the two spectra.

(2) There are two absorption spectra (*a*) that which is the reversal of the bead spectrum and may be regarded as identical with the bead spectrum in the sense that reversing spectra in general are identical. (*b*) the absorption spectrum of neodymium in aqueous solution (table II). This latter shows no obvious sign of identity with either emission spectrum there being but three coincidences (1589, 2014 and 2107) and of these 2014 and 2107 are really coincidences of absorption bands since they could be located in the bead spectrum only in this reversed condition.

TABLE I

EMISSION SPECTRA OF NEODYMIUM OXIDE

BULK SPECTRUM				BEAD SPECTRUM			
SET A		SET B		SET A		SET B	
$1/\mu \times 10^3$	INTERVAL	$1/\mu \times 10^3$	INTERVAL	$1/\mu \times 10^3$	INTERVAL	$1/\mu \times 10^3$	INTERVAL
1441(0)		1651(0)		1589(0)		1355(?)	
	18.5×2		18.5×6		18.5×8		18.5×9
1478(0)		1762(0)		1737(0)		1521.5(+.5)	
	18.5×2		18.5×12		18.5×8		18.5×7
1515(0)		1984(0)		1885(0)		1651(0)	
	18.5×2		18.5×6		18.5×7		
1552(0)		2095(0)		2014.5(−0.5)			
	18.5×2				18.5×5		
1589(0)				2107(0)			
	18.5×6						
1700(0)							

Numbers in parentheses denote departures from precise coincidence with the value of the corresponding member of the set to which the bands belong. As these are never more than one unit, while the distance between sets is of the order of six units, there is never any question as to which set a band should be assigned. Positions of bands in table II are those given by Kayser except in the case of two marked (A) in which the values are those of Auer, and those marked (N) which were located by the author in the reversal of the bead spectrum.

The *identity of structure* in this case also comes out in the fact that all the bands (29) in table II can be arranged as members of the sets A and B and of a third set C which has the same frequency interval and is obtained by shifting set B five and a half places towards the violet. Table II includes all the neodymium absorption bands listed by Kayser and the positions are those given by him except as otherwise indicated. It is believed

that the relation here described is common to all banded spectra of emission and absorption but that it is usually concealed by the overlapping of the components.

TABLE II

ABSORPTION SPECTRA OF NEODYMIUM

SET A		SET B		SET C	
1570.5(+0.5)		1355(0)		1452.5(±1.)	
	18.5×1		18.5×1		18.5×1
1589(0)		1373.5(+0.5)		1471(+1.)	
	18.5×1		18.5×9		18.5×1
1607.5(+0.5)		1725(−1.)A		1489.5(+0.5)	
	18.5×7		18.5×1		18.5×6
1737(0)		1743.5(+0.5)		1600.5(−0.5)	
	18.5×9		18.5×12		18.5×6
1903.5(+0.5)		1965.5(−0.5)		1711.5(+0.5)A	
	18.5×2		18.5×6		18.5×1
1940.5(−0.5)		2076.5(±1.)		1730(−1.)	
	18.5×4		18.5×3		18.5×1
2014.5(−0.5)N		2132(0)		1748.5(+0.5)	
	18.5×5		18.5×3		18.5×7
2107(0)N		2169(0)		1878(+1.)	
	18.5×8				18.5×2
2255(?)				1915(+1.)	
					18.5×3
				1970.5(−0.5)	
					18.5×7
				2100(+1.)	
					18.5×11
				2303.5(+0.5)	
					18.5×5
				2396(−1.)	

[1] Bunsen: *Liebig's Annalen*, **131**, p. 255 (1864).
[2] Bahr: *Ibid.*, **135**, p. 376 (1865).
[3] Nichols and Howes: *Physic. Rev.* (2) **19**, p. 313 (1922).
[4] Tanaka: *J. Optical Soc. Amer.*, **8**, p. 287 (1924).
[5] Nichols and Howes: *Ibid.*, **6**, 42 (1922).
[6] Kayser: *Spectroscopie*, Bd. III, p. 446.

HALOGEN ISOTOPES AND INFRA-RED REFLECTION SPECTRA

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Communicated December 9, 1924

As a result of an investigation on the selective reflection from inorganic salts, it was shown by the writer[1] that all sulphates studied showed bands near 9.05μ in the infra-red. Likewise, all nitrates studied showed a characteristic band near $7.40\ \mu$. From these observations it was concluded that the resonating mechanism, responsible for these bands of selective reflection, was localized within the negative ion. Since solutions as well as crystals showed such bands, it is believed that the negative ion retains its identity throughout. Later investigations by Morse,[2] Coblentz[3] and others have completely verified the above conclusions.

Recent work on the structure of crystals and conjectures as to the character of interatomic forces have renewed the interest in the above subject. Of immediate interest is the subject of isotopes. The line of reasoning followed is briefly, as follows: since infra-red reflection maxima are usually complex due to the multi-atomic character of the negative ion and to double refraction, it seemed desirable to limit the considerations to the halogen salts of the alkali metals. Of these, the salts of potassium have been investigated for selective reflection in the region of long wave-lengths by Rubens.[4]

Now, Aston[5] has showed that Cl consists of a mixture of isotopes of atomic weights 35 and 37, Br has isotopes of atomic weights 79 and 81 while I is "pure" with the single atomic weight of 127. Comparing these data with Rubens' results it develops that each halogen salt of potassium has as many bands of selective reflections as there are isotopes, i.e., KCl has 2, KBr has 2 and KI has 1. The numerical values are shown in the following table:

	ATOMIC WTS. OF ISOTOPES		BANDS OF SELECTIVE REFLECTION λ	$\frac{1}{\lambda}$
K *Cl*	35	Cl	62.0μ	161
	37		70.3	142
K *Br*	79	Br	75.6	132
	81		86.5	115
K *I*	127	I	96.7	103

Since the wave-lengths of the bands increase with increasing atomic weight of the negative ion it seemed reasonable to associate the lighter isotopes with the band of shorter wave-length. Upon plotting wave-lengths against atomic weights, curves of an indecisive character were

obtained. By plotting, however, wave-numbers ($1/\lambda$) against atomic weights, the series of straight lines, shown below resulted. (Fig. 1.)

While the writer is not familiar with any theoretical work having a bearing on these observations, it does appear that the character of the curves is too striking to be without significance. First, it is evident that the curve for the heavier isotopes is parallel to that for the lighter. Incidentally, iodine lies on the same curve as the lighter Cl and Br isotopes. This might be interpreted as being the configuration of greatest stability.

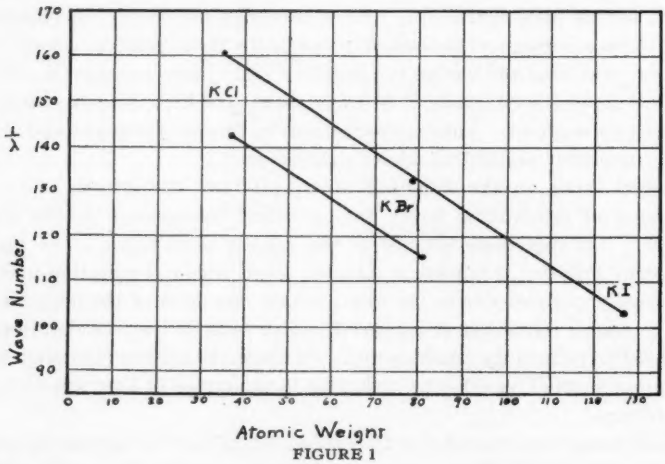

FIGURE 1

If atomic weight alone came into play here, it might be conceived that all points would lie on the same line—such as the upper. In that case, a change in atomic weight from 37 to 35 (Cl) would bring about only a very small change in the wave-length of the reflection maximum. The actual change is, however, large. Granting that all the preceding speculations are true, it would appear that the change in vibrational frequencies brought about by a nuclear loss of two protons and two electrons is much greater than the mere change in atomic weight would seem to justify.

Another point of interest is suggested by Rubens' results for NaCl and KCl. His curves are reproduced on the following page. (Fig. 2.)

If it be true that the short wave-length maximum is due to the lighter isotope, then it appears that because of the reversal of heights of the two maxima for rocksalt and sylvite, the isotope 37 is most abundant in rock salt while isotope 35 is most abundant in sylvite. Experiments are in progress to find samples of these two crystals which show the above reversal in intensity. Molecular weight determinations of the Cl derived from these two samples ought to show a difference.

It is, of course, entirely possible that these differences in the reflection maxima are to be ascribed to the fact that, while NaCl[6] crystallizes as a face center cubic lattice, KCl crystallizes as a simple cubic lattice.

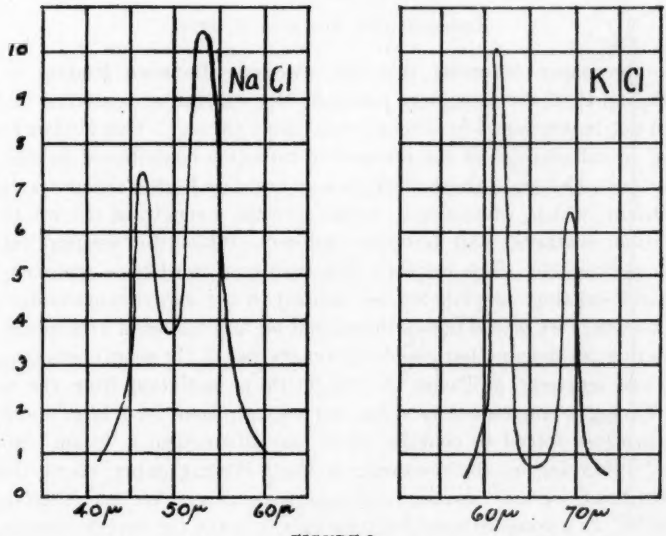

FIGURE 2

It is not without possibility that isotopy might be revealed in still another manner. Morse[2] has pointed out from his study of carbonates, that, while their reflection maxima lie very approximately at the same wave-length, there is a slight shift toward longer wave-lengths with increasing atomic weight of the positive ion. If, therefore, salts having an isotopic positive ion are studied, a complexity of the reflection maximum ought to result from this cause, also. Experiments are being undertaken to test this point.

[1] Pfund. *Astrophys. J.*, Nov. 19 (1906).
[2] Morse, *Ibid.*, July 26, 225 (1907).
[3] Coblentz, *Investigations of Infra-red Spectra* (1906), Carnegie Inst. of Wash.
[4] Rubens and Hollnagel, *Verh. D. Phys. Ges.*, **8**, 83 (1910).
[5] Aston, *Isotopes* (Edward Arnold and Co.)(1922).
[6] Bragg., *X-Rays and Crystal Structure*, p. 91 (Bell and Sons) 1924.

THE COMPTON EFFECT WITH NO BOX AROUND THE TUBE

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In the paper following this one, evidence discussed leading to the conclusion that the Compton peaks in the spectra of scattered X-rays could not be explained by Duane's box-effect theory. This evidence consisted in calculations of the amount of radiation contributed by the box in various cases, and the calculations were based on Barkla's mass scattering coefficient, which, we assumed, would give the strength of the whole box radiation, scattered and tertiary together. While this assumption appears permissible, since Barkla's measured rays must have included any tertiaries existing, nevertheless we decided to try experiments under conditions where we would not be dependent on any values of absorption and scattering coefficients, but could rely on the size of the room containing the tube and scatterer, as Duane did, to get rid of radiation from the walls. Not having a convenient location, nor enough lead, for a large room, we are therefore forced to consider what may distinguish a "room" from a "box." Relying on the reasoning in the following paper about doubly shifted lines, we may assume no second scattering. We may then define a "room" as a compartment large enough to make the inverse square law alone suppress the scattered rays from light elements beyond detection, even if the light elements in question return all the rays falling on them from the tube. This definition does not require a very large room. If, for example, the scatterer is 6 cm. from the target and the nearest light atoms struck by the direct rays are 140 cm. away, as in the experiment to be described, then the inverse square law alone will reduce the returned rays to less than $(6/140)^2$, or 0.0018, of the fraction of the primary rays striking such atoms. And whatever may be said about scattering and absorption coefficients, the limitation by the inverse square law cannot easily be denied.

The room used was the one shown in fig. 1. The tube was supported by an iron clamp standing on the low table, about 30 cm. high, that held the iron water tank. The clamp held the end of the anticathode outside the glass, and the cathode wires hung from near the ceiling. Thus there were no insulators supporting the tube nearer than the table, which was 90 cm. below it, and all rays that might strike the table, the clamp, the water tank, or any light elements nearer than the ceiling and the corners of the room were stopped by a large lead shield. This shield, being curved, is difficult to show on the diagram, but it was at least 20 cm. from the sulfur everywhere. Furthermore the sulfur, being 1.0 cm. thick, with an absorption

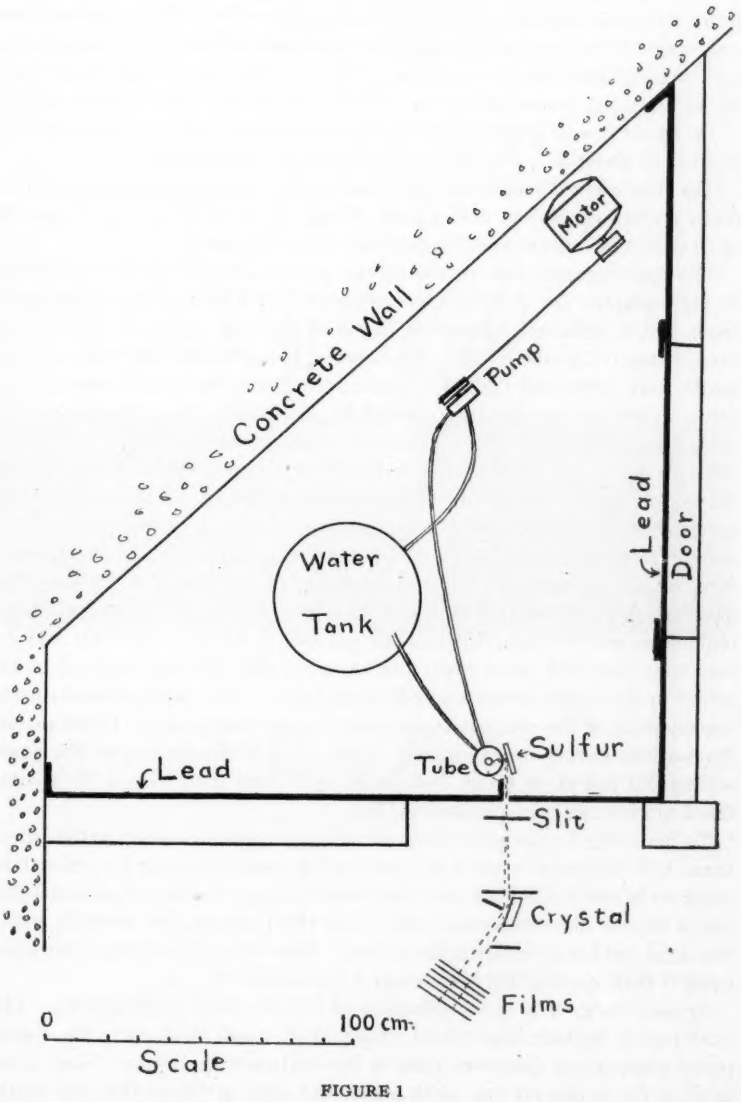
Concrete Wall
Motor
Pump
Water
Tank
Lead
Door
Lead
Tube
Sulfur
Slit
Crystal
Films
0
100 cm.
Scale

FIGURE 1

coefficient[1] of about 18 cm.$^{-1}$, is perfectly opaque to these rays and shields everything behind it. It was supported entirely from behind by a glass tube, protected from direct rays by the opacity of the sulfur. Special care was taken to be sure that no glass or other material containing oxygen or carbon could send any rays to the crystal, and that no primary rays could strike anything visible from the crystal except the sulfur. The surface of the sulfur was so placed that the rays to be used struck it at about 60° and left at about 30°, making a scattering angle of about 90°.

The tube was a standard molybdenum target Coolidge tube, run on A. C., doing its own rectifying, with a peak voltage of about 50 kv. and a current of 20 to 30 ma. Exposures ranged from 30 to 222 hours.

The spectrograph was an ionization spectrometer adapted temporarily to photographic use. It therefore covered only a short range of the spectrum, but a sufficient range, the limits of glancing angle, at the setting used, being 6°33′ and 8°25′. The crystal being calcite, the wave-length limits were 0.692 and 0.886Å. These were determined by removing the sulfur, inserting another tube carried by clockwork across the line of the slits, photographing a direct spectrum and measuring its limits and the distances involved. This was superposed on the upper third of each photograph, the lower two-thirds being covered with lead. The spectrograph held nine films, supported without mutual contact, to allow the removal and development of any film without disturbing the others. This arrangement enabled us to take films with a variety of exposures, to put the comparison spectrum on some and not on others, to identify reflections from oblique layers of atoms, such as the patches in fig. 2 marked *O*, and be sure they were not stray rays, and to make sure nothing was lost or inserted by any imperfections in individual films. The slight irregularities in the intensity of the comparison spectrum in fig. 2 were due to tube-current fluctuations during its exposure. Other comparison spectra at the same setting did not show them, and could have been used here if their scattered spectra had been exposed as long.

To make the Duane peak show as well as it would in an ionization spectrum, it is necessary to use a wide slit and a resolving power low enough to make no better distinction than the ionization spectrometer between a line and a narrow but continuous peak. For this purpose, the resolving power was kept too low to separate the α lines. They would have been just separated if their spacing had been about 1.5 of what it is.

Results.—Fig. 2 is a reproduction of one of these photographs. The unshifted α doublet, unresolved, shows at *A*, much stronger in the superposed comparison spectrum than in the scattered spectrum. Next to it, at *C*, is the Compton line, with about the same intensity that one would expect from all the earlier work such as Ross's photographs with aluminum and copper. Its position agrees with the computed position to within the

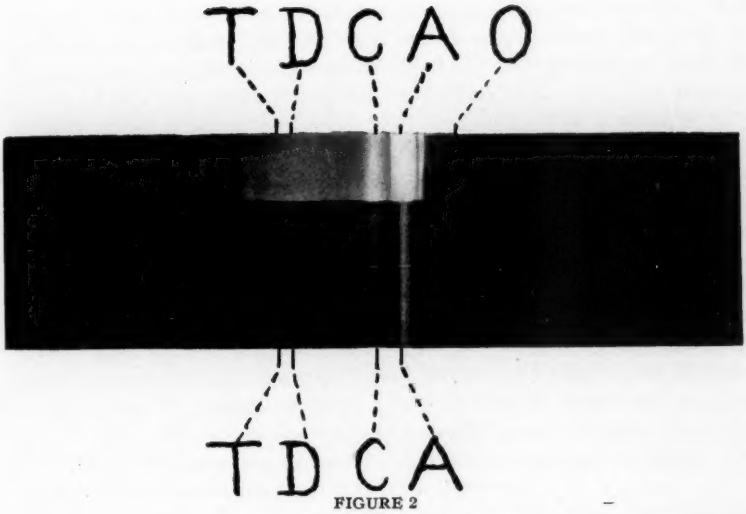

FIGURE 2

limits of experimental error, about 0.0010 to 0.0015Å, or say 5 per cent of the Compton shift. At D is the place where Duane's peak ought to be, judging by his own data in these PROCEEDINGS, April, 1924, where his peak is exactly 60 minutes from his α peak. No line appears there in any of these photographs, although in some of them the exposure was long enough to bring out the continuous spectrum, and was 5 or 10 times as long as was needed to bring out the line C.

In Duane's paper on the box experiment he shows a line without the box, of about the intensity of line C, judged relatively to α, and ascribes it to the tertiary rays of frequencies $(MoK\beta - SK)$ and $(MoK\alpha - SL)$. If these lines exist, as his theory demands, $(MoK\alpha - SK)$, at the point D, should be almost as much stronger than the former of them as $MoK\alpha$ is stronger than $MoK\beta$, that is, about 4 times, according to Wooten.[2] And it should be stronger than the latter in the same ratio in which the K absorption exceeds the L in sulfur, say about 8. Consequently, it should be about 2.7 times as strong as the sum of the lines at C. The fact that it is not detectable at all in the longest exposures means that it must be very much fainter than the line C, and prohibits this explanation of the line C.

As to the position of the theoretical D line, there may be some question. The position shown here is taken directly from Duane's own paper, and is doubtful only because of a statement in that paper to the effect that it agrees with his theory. The theory demands a short-wave limit 67′ from the α peak, or 7′ beyond this exerimental peak. The theoretical peak is still further beyond. The best way to find out exactly how far beyond is perhaps to start from his explanation of the C peak, which is 7′ from its theoretical short-wave limit, and assume the $(MoK\alpha - SK)$ peak to be the same distance from its theoretical limit. This calculation would put the peak at T, which is well within the limits of this photograph, even at the upper end of the comparison picture, and owing to the obliquity of the edges of the calcite, still further within the limits at the lower end.

The fact that the line D is not there leaves the line C as a definite confirmation of Compton's predictions, with which Duane and his collaborators disagreed in the statement quoted in the first paragraph of the following article. Also, it proves that under these conditions at least, the Duane line must be very much weaker than the Compton line if it is present at all.

Width of Scattered Lines.—The early work of Compton and of Ross indicated that the scattered lines were broader than the primary and in particular that the modified line was much broader and less sharply defined than the unmodified. In fig. 2 it is shown that the unmodified scattered line has sharp edges and is of the same width as the primary line to within a small fraction of a minute. The small increase in width and lack of sharpness in the modified line is no more than would be expected from the small but unavoidable lack of homogeneity in the scattering angle.

The Present Status of Tertiary Ray Theory.—Applying these results to present theories, obviously no change is required in Compton's. With regard to tertiary ray theory, however, the case is different.

Three tertiary-ray theories that have come to our attention are those of Clark and Duane, Webster,[3] and Compton.[4] It has been pointed out by Compton,[4] Webster[3] and Gray,[5] that the Clark and Duane theory fails to account for any radiation approaching the intensity of the rays they observe, even as to order of magnitude; and Webster[3] has shown also that their hypothesis of filtering fails as completely in accounting for the narrowness of the peaks.

Webster's theory was stated with two alternative forms, either of them covering these two points, but one giving the same short-wave limits as the theory of Clark and Duane, and the other slightly different limits, which agree better with a set of experimental limits derived from a slightly different method of handling their data. There is still some difference of opinion on this question of short-wave limits, but in view of the fact that Clark and Duane, in discussing it, made no mention of the questions of intensity and narrowness of the bands we may take the necessity for some such innovations as Webster's theory or Compton's for granted.

The most important point in these innovations was a new hypothesis, that there was an unprecedentedly strong probability of emission of a quantum of tertiary rays from the photoelectrically active atom during the process of ejection of the electron. These rays are, of course, independent of the fluorescent rays emitted later. Since this hypothesis was made *ad hoc*, to overcome the intensity difficulty, and was justified by only one additional success, namely on the question of narrowness of the bands, it owes its existence entirely to Clark and Duane's tertiary ray spectra. If all such experiments had given results like ours, therefore, it would never have been made and the absence of tertiary radiation would not have been at all surprising.

The point that is most surprising is that one set of experiments seems to confirm this hypothesis and the other to deny it. If it were any hypothesis about molar processes, molar differences in apparatus might make this discrepancy. But how can any difference in apparatus, such as we have here, make a difference like this within the atom?

Each set of experiments, nevertheless, is very self-consistent, though covering wide ranges of substances and wave-lengths, and each set obeys simple laws and obeys them without any very well established exceptions. It is, therefore, very difficult to believe either set to be due to experimental errors, especially in view of the simplicity of the experimental conditions and the consequent lack of chances for unforseen factors. A complete theory of this phenomenon must contain some account of the conditions determining the presence and intensity of tertiary rays. It is to be hoped that further

experiments, on which we are now working by both photographic and ionization methods, will suggest some way to clear up this puzzling situation.

NOTE: Since this paper was written we have built another spectrograph, of quite a different design, in a different part of the room, using a different molybdenum tube and a scatterer of a different element, aluminum. The photographs are even better than those with sulfur, and show the α and β lines, in both the first and second orders, each with its Compton-shifted line about equal in strength to the unshifted line. The continuous spectrum shows also, at least in the first order, but there is not the slightest trace of a tertiary line.

[1] Calculated from Bragg's N^4 law on the basis of Barkla's value of the absorption coefficient of aluminum.

[2] B. A. Wooten, *Physic Rev.*, **13**, 71–87, Jan., 1919. This ratio is for the rays after emergence from his tube.

[3] D. L. Webster, these PROCEEDINGS, **10**, 186–190, May, 1924.

[4] A. H. Compton, *Physic. Rev.*, **24**, 168–177, Aug., 1924.

[5] J. A. Gray, *Brit. Assoc. Adv. Sci.*, meeting of Aug., 1924.

COMPTON EFFECT: EVIDENCE ON ITS RELATION TO DUANE'S BOX EFFECT

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In the September number of these PROCEEDINGS, Duane[1] and several of his collaborators published two papers describing experiments on secondary X-rays, with a wooden box which could be put around the tube and secondary radiator and removed again without disturbing the rest of the apparatus. They find in these experiments that with the box in place they obtain a peak in the spectrum similar to the peaks found by other observers and explained by the Compton theory, but when the box is removed, the peak disappears. This effect they explain as a result of tertiary rays from the wood, and they draw the conclusion: "These experiments indicate that, if we look at X-radiation from the point of view of the emission of radiation quanta, having a certain amount of energy and momentum, we must assume that the momentum and energy are transferred not to single electrons but to atoms and groups of atoms, substantially as represented in a theory recently published on the transfer of radiation momentum to matter in quanta."

The purpose of this paper is to discuss further evidence on this matter, leading us to doubt this conclusion. Some of this evidence is obtained from

calculations from Barkla's data on scattering. The rest is from certain aspects of Ross'[2] experiments which were not discussed in his earlier papers, but which have taken on a new importance because of the paper quoted on preceding page.

With regard to the cause of their "box effect," Duane and his collaborators make the statement; "No one can doubt that a considerable amount of X-radiation must be passing in all directions through a box of the kind described, containing an X-ray tube in action. This radiation must have the wave-lengths characteristic of the secondary and tertiary radiation belonging to the chemical elements composing the walls of the box and whatever there is inside of it." Without at this point discussing such doubts although we have them for the cases in question, we must note the fact that if such secondary and tertiary rays from one part of the box strike another part, they will give rise to quaternary rays, and rays of still higher order, with wave-lengths shifted from the primary, not only by the amount given by a single application of Duane's tertiary wave-length equation, but by a second such shift, and more. Consequently if such rays are to be considered, such doubly and triply shifted peaks must be looked for in the spectra. On one of their published spectra, for molybdenum rays scattered from sulfur, the singly shifted peak is slightly stronger than the unshifted, even after a deduction for their β-line and sulfur L series effects. This would indicate that the singly shifted rays from the box are actually slightly stronger than the primary at the scatterer, and presumably also at almost any part of the box. The doubly shifted rays therefore should arise from a source as powerful as that of the singly shifted rays, and should be equally strong. But the doubly shifted peak does not appear at all.

This in itself contradicts their theory when carried to this logical conclusion. Moreover, it permits us to calculate the box effect without making any allowance for more than one scattering of any one quantum by the box.

An exact calculation of the amount of radiation returned by the box, even with only single scattering or single tertiary re-emission, is complicated by many minor factors which, so far as questions of order of magnitude are concerned, may as well be neglected. For a rough calculation, then, we may assume Barkla's well known mass-scattering coefficient, 0.2 cm.^{2}/gm., to represent the strength of all re-emitted rays, scattered and tertiary, and neglect all non-uniformity of their space distribution and all increase of absorption by obliquity of incidence and emergence in the walls of the box. With these simplifications, it appears that the radiation returned by the wall on the side of incidence is the same as that emitted by a new source of rays whose total emission bears a ratio to the total flux of energy striking the wall, equal to $(\sigma/2\mu)\ (1 - e^{-2\mu T})$, where σ and μ have the usual meanings and T is the thickness of the wall. This formula, applied to the case of the human

body subjected to very penetrating rays, gives results of the order of magnitude to account for the experimental evidence quoted by Duane and his collaborators in support of the quoted statement about scattered rays; and calculations on a similar basis account readily for the scattered rays on the emergent side, also mentioned in this connection. Applied to the present case, however, with a box of thickness $T = 2$ cm. (an estimate from their diagram) and with $\sigma/\rho = 0.2$ cm.^{2}/gm. and $\mu/\rho = 0.86$ cm.^{2}/gm. (the latter being the mean of values given by Olson, Dershem and Storch[3] for carbon and oxygen), the fraction in question is only 0.10. Moreover, since rays can leave the target only on the forward side, the flux of energy to be multiplied by this factor is only half the radiation produced in the target. Consequently, if these data are correct, the box as a whole should act as a source not more than 0.05 as strong as the target.

As the walls of the box are on the average considerably further from the block under examination (the "scatterer") than the target is, and most of the illuminated part of the walls is back of the scatterer, the rays received from the box by its front face should be very considerably less than 0.05 of those received from the target, and the box-effect peak in the spectrum of its rays should be correspondingly weak as compared to the peak of the primary wave-length. As the observed box-effect peak is actually at least as strong as the other, this leads us to believe that Duane's experiments demand some other explanation.

The experiments of Compton and Woo[4] likewise, show peaks of the same order of intensity in the Compton-shift position, which cannot be explained on such a basis and for which Compton's theory seems to be the only explanation yet at hand.

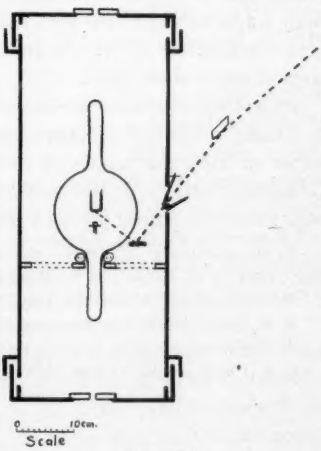

FIGURE 1

In Ross' experiments with the exception of one case, fig. 8 of his paper in these PROCEEDINGS, July, 1924,[2] there is still another factor in the situation. For in all but this one of his numerous experiments, he used the box shown in fig. 1, containing no wood. The only materials in this box containing any light elements were the tube itself, the lead-glass top and bottom plates, the hard-rubber plate holding the tube, the scatterer and its paraffin supporting post. Of these, the lead-glass plates were in the shadows of the target and the cathode, respectively; and all the others except the tube itself were back of the scatterer, which was opaque to these

rays, and therefore they could not send any rays to the surface under examination, except by a second scattering. As the combined strength of the rays from the two pieces in question, the hard-rubber plate and the paraffin post, was only about 0.02 of the strength of the primary rays, and the lead walls would return only about 0.0005 of the rays of this frequency striking them, the maximum strength of tertiary rays from light elements that could be directed in this way toward the top of the scatterer is 0.00001 of the radiation from the source, even without any allowance for the effect of increased distance. Ross' experiments must therefore be free from any detectable trace of the "box effect."

The only light atoms that might conceivably influence his experiments are the oxygen atoms in the glass of the tube. Approximate calculations show that their effect might possibly amount to a few per cent if the scatterer was in direct contact with the tube. The calculations are complicated by the phenomena of excess scattering, and the best way to determine the influence of the glass is by experiment. Fortunately the data are readily available, in Ross' photographs with graphite, in the paper quoted above. If the glass sent any appreciable tertiary rays to the scatterer, there would be the same doubly shifted peak discussed above. Careful examination of Ross' original negatives, even ones with strong Compton lines, such as fig. 8 of that paper, fails to reveal any such doubly shifted lines.

Finally there is one more line of evidence, namely the fact that in Ross' photographs of the carbon-scattered rays at various angles, the shifted line changes its position exactly according to Compton's theory, and much more than could be explained by Duane's hypothesis of filtering;[5] and that for rays scattered at 30° it is actually on the short-wave side of Duane's theoretical short-wave limit.

Altogether, the evidence reviewed here seems to us definitely contrary to Duane's box-effect theory as an explanation of the Compton peaks, either in his experiments or in those of Compton and Ross, and leaves Compton's theory of the scattering of quanta by single electrons as the only theory advanced yet that will explain them.

[1] A. H. Armstrong, W. Duane and W. W. Stifler, these PROCEEDINGS, **10**, 374–378, Sept., 1924; S. K. Allison, G. L. Clark and W. Duane, *Ibid.*, 379–384.

[2] P. A. Ross, *Ibid.*, **9**, 246–248, July, 1923; **10**, 304–306, July, 1924.

[3] A. R. Olson, Elmer Dershem and H. H. Storch, *Physic. Rev.*, **21**, 30–37, Jan., 1923.

[4] A. H. Compton and Y. H. Woo, these PROCEEDINGS, **10**, 271–273, June, 1924.

[5] G. L. Clark and W. Duane, *Ibid.*, **9**, 413–424, Dec., 1924.

THE NATURE OF THE ASSOCIATION BETWEEN ANTHOZOA AND ZOOXANTHELLAE[1]

BY H. BOSCHMA

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There are two conflicting opinions concerning the nature of the food of reef-corals. One of these is defended chiefly by Vaughan and reads thus: "The food of reef-corals consists solely of animal matter." This statement was made after elaborate feeding experiments on a large number of different species of West Indian reef-corals. These polyps invariably refused to eat plant material (diatoms and sea-weeds) which was offered to them. The other opinion, first advocated by Gardiner, is that the food of reef-corals consists in large part of the zooxanthellae which live in great abundance in their entoderm. The principal evidence for this view lies in the fact that the food-remnants found in the gastric cavity of living coral-polyps always contain a large number of zooxanthellae in various stages of disintegration, as the result of digestive action on them.

One of the ways to obtain direct evidence that coral-polyps derive a part of their nourishment from their symbiotic algae is to compare the phenomena of digestion in reef-corals which possess zooxanthellae, with those in nearly allied species which have none. While there is considerable evidence as to the rôle of the zooxanthellae which is the result of incidental study, there remains much to be done in the way of experimental work to show what happens when polyps with symbiotic algae are deprived of other food or are supplied with it in more than normal abundance.

Astrangia danae is the only madreporarian coral found on the northern shores of the Atlantic coast of North America, and, as is well known, this dimunitive form does not occur north of Cape Cod. This species, which I came to the Marine Biological Laboratory at Woods Hole to study, proved to be a favorable object in which to follow the process of digestion. Usually the polyps of this species are completely devoid of zooxanthellae and their tissues, which have no pigment of their own, are therefore quite transparent. Occasionally, however, in colonies of this species zooxanthellae do occur, on account of which the polyps acquire a more or less brownish hue.

In the gastric cavity of freshly collected specimens there are often found remnants of partially digested food consisting of small planktonic organisms. But, in addition, there were always found in the brown polyps zooxanthellae or products of their disintegration, whereas these algae never occurred in the food-remnants of the colorless polyps.

The polyps of *Astrangia* readily ingested food, which in my experiments usually consisted of crab-meat. In order to trace the food in the internal

organs after it had been swallowed, it was usually colored with litmus. After a few hours the meat had vanished from the gastric cavity, for it had been digested by the mesenterial filaments. The evidence for this statement is the fact that next to the margin of the mesentery, which contains a great number of nematocysts, there is a zone which, some time after feeding, was full of red vacuoles, though before feeding this zone contained no such vacuoles. This indicates that the meat had been ingested in this region and that the reaction in the vacuoles was acid. More than two days elapsed before the color in the vacuoles changed to blue, but thereafter the greater part of the vacuoles gradually assumed that color, which showed that the reaction had become alkaline.[2]

That zone of the mesenterial filaments where, in the colorless polyps, the red vacuoles were found after artificial feeding, exhibited in brown polyps an abundance of zooxanthellae. These algae, however, were in a less healthy state than those in the entoderm of the other parts of the polyps. Some appeared quite normal, but in the greater part of them the contents had undergone changes in color and arrangement. Since they are found in the region where food of extraneous origin is ingested, these changes are undoubtedly due to their being in process of digestion by the coral-polyps.

When crab-meat is given to the polyps of *Astrangia* which contain zooxanthellae in their entoderm, it is as readily ingested as by those which have none. In the course of a few hours after meat colored with litmus has been fed, red vacuoles are seen among the zooxanthellae in the mesenterial filaments. After very abundant feeding of animal matter the zooxanthellae slowly (in a few days) disappear from the zone of digestion. Those algae which were already ingested have been completely dissolved, but no fresh algae are taken in by the mesenterial filaments when sufficient food from another source is available.

Since zooxanthellae are but rarely found in *Astrangia*, the digestive phenomena observed in this species cannot be considered, without further evidence, as applicable to all Madreporaria. The opportunity to work at the Bermuda Biological Station for Research, where there are many species of coelenterates in which the entoderm harbors symbiotic algae, offered an opportunity of pursuing this problem on a wider range of material. Owing to the limited time at my disposal for these studies, the four following species were selected for experimentation, as they were close at hand and easily controllable:

Isophyllia dipsacea, Siderastraea radians, Zoanthus sociatus, and Condylactis passiflora.

In *Isophyllia* and *Siderastraea*, both of which are true reef-corals, the phenomena of digestion are on the whole the same as those in the brown polyps of *Astrangia*. In the mesenterial filaments of freshly collected specimens of both species a zone is found, immediately back of the free

edge, where numerous zooxanthellae are being digested. Here, as in *Astrangia*, all the different stages in the disintegration of the algae are present.

When animal matter (in this case mussel-meat, or mussel-juice, colored with litmus) was fed to the polyps it was digested in the zone of the mesenterial filaments where the partly disintegrated zooxanthellae are found. A few days after food had been abundantly supplied, a striking fact was observed, viz., that the number of zooxanthellae in the zone of digestion had considerably decreased. Consequently it is reasonable to suppose that in these species, too, the nutrition afforded by the animal matter is quite sufficient for the polyps and that there is no longer need of ingesting fresh zooxanthellae.

As for *Zoanthus* the polyps refused to ingest any kind of extraneous food that I offered to them, so that my studies were limited to a few observations on the mesenterial filaments in the normal state. The part of these filaments adjacent to the edge containing the nematocysts are here, as in the other Anthozoa hitherto studied, the chief digestive organs; these parts here also contain large numbers of zooxanthellae, many of which are in an advanced stage of disintegration. If further experiments, conducted with a large variety of food materials, were to give, like mine, negative results in all cases, it would be safe to conclude that *Zoanthus* is even more dependent on symbiotic algae for its sustenance than most other polyps are:

In the case of *Condylactis* it was found that the mesenterial filaments contained, in the usual region, large numbers of zooxanthellae, which were in various stages of disintegration. But my available time was not sufficient to allow me to carry on satisfactory experiments to test the influence on the zooxanthellae of feeding the polyps with extraneous food.

The observations and experiments described above show that the association of zooxanthellae with the forms studied is substantially a case of parasitism in which the polyps feed on the algae. The algae probably derived some profit from living in the tissues of the polyps (they are more or less sheltered, and in a position favorable for the action of light, which they need for assimilation; perhaps they may also use the nitrogenous waste products of the polyps), but the final result of the association is that a large number of the zooxanthellae are digested by the coelenterates. In nature the food-supply for the polyps from their surroundings seems too scanty (in fact many authors have commented upon the scarcity of planktonic organisms in the water of warmer seas), and therefore the polyps are largely dependent upon their yellow algae for sustenance.

[1] From the Marine Biological Laboratory, Woods Hole, and Contributions from the Bermuda Biological Station for Research. No. 146.

[2] Probably in all coelenterates this change from an acid to an alkaline reaction takes place very slowly. Most authors (e.g., Metschnikoff, Mesnil) knew and stated that during digestion, in actinians, the reaction of the vacuoles is acid: but Jordan was the first to suggest that probably this acid period was followed by an alkaline one, during which the absorption of the food took place.

THE MECHANISM OF REACTIONS IN THE UREA SERIES

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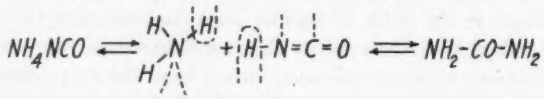
Read before the Academy November 11, 1924

Except for known reactions between ions and the corresponding dissociation of molecules into ions, chemical reactions in general—without prejudice to the electrical nature of chemical affinity—appear to take place between molecules. Of the reactions between molecules two sorts appear to be distinguishable, one in which metathesis occurs or the interchange of parts between two or more molecules, and the other in which the spontaneous combination or un-combination of molecules occurs directly. Reactions of the second sort may be reversible, like the combination of ammonia with hydrogen chloride, or irreversible, like the addition of bromine to ethylene, or the molecule first formed by the combination of the original molecules may break down again to yield molecules different from those from which it was first formed, as in the case of ammonium nitrate which is formed by the combination of ammonia with nitric acid and which yields nitrous oxide and water when it is heated.

At present there is a growing tendency among organic chemists in favor of the belief that there are no real metathetical reactions strictly so-called, that reactions consist of the spontaneous addition and separation of molecules, and that the appearance of metathesis which exists in many cases is due to the readiness of the molecule first formed from the reagents to break down again in a new sense to yield the products of the reaction. Such mechanisms have been proved in particular cases, such as in certain halogenations; they have been shown to be highly probable in others, such as in ester formation; but in many other cases, probably the large majority, they are hypothetical and unconvincing.

In the urea series we have been able to show that the mechanism of a large number of reactions is either the reversible combination of molecules or the direct combination of molecules to form new molecules which themselves break down in a predictable manner. By applying the end products as reagents it has been found possible to simplify a number of syntheses.



Ammonia and cyanic (or isocyanic) acid enter into reversible combination with one another in two ways which correspond to the two-fold chemical characters of these substances. If the ammonia functions in its basic

nature, the nitrogen increasing its valence to five, and if the ionizable cyanic acid acts as acid hydrogen and electronegative cyanate radicle, then the product is ammonium cyanate. If the ammonia acts in its other capacity of H and NH_2, and if the cyanic acid functions through the unsaturated character of its nitrogen-carbon linkage, then urea is the result.

The conversions of the cyanates of ammonium and of primary and secondary amines to urea and substituted ureas by the evaporation of their aqueous solutions have long been cited as examples of the "urea rearrangement." It seems proper and convenient to denominate the reverse of such changes the *urea dearrangement* and to say that a urea derivative *dearranges* when its molecule breaks down in an orderly fashion analogous to that in which urea breaks down into ammonia and cyanic acid. Just as the possibility of urea formation is determined by the presence of one unsubstituted hydrogen in the ammonia residue, so the possibility of the dearrangement is determined by one unsubstituted hydrogen in the urea molecule. The mechanism of the reactions is not affected by the substitution of the oxygen of the cyanic acid. Unsymmetrical urea derivatives, if they have hydrogen atoms on each of the nitrogens, dearrange in two modes which correspond to the movement of one or of the other of the hydrogen atoms.

When urea is heated alone[1] or in aqueous solution[2] it dearranges into ammonia and cyanic acid. The ammonia escapes, and if aniline is present the cyanic acid combines with it to form phenylurea. Phenylurea dearranges in two modes which correspond to two methods for its formation.

$$C_6H_5NH_2 + HNCO \rightleftarrows C_6H_5\text{-}NH\text{-}CO\text{-}NH_2 \rightleftarrows C_6H_5NCO + NH_3$$

If it is heated alone at 160°, ammonia comes off rapidly, the aniline and phenylisocyanate may be detected by their odor but they combine in large part to form *sym.*-diphenylurea which crystallizes out from the hot liquid, and cyanic acid may be detected by means of silver nitrate in the water with which the apparatus is washed out after the experiment. When an aqueous solution[2] of phenylurea is distilled, aniline may be detected in the distillate and *sym.*-diphenylurea crystallizes from the boiling liquid. By heating urea with the amine or with its hydrochloride[2] at 160°, or by refluxing urea in aqueous solution[3] with the amine or its hydrochloride, we have prepared *sym.*-di-*o*- and *p*-tolyl, di-α- andβ-naphthyl, dimethyl, di-*n*-butyl, di-*n*- and *iso*-amyl and dibenzylureas in satisfactory yield.

The dearrangement of phenylthiourea may be demonstrated very simply by heating a small quantity of the material in a test-tube. It undergoes a violent decomposition slightly above its melting-point, the odors of ammonia, of aniline, and of phenyl mustard oil may be detected, and the residue which consists largely of *sym.*-diphenylthiourea gives with ferric chloride the red color characteristic of thiocyanic acid.

Symmetrical disubstituted ureas in which the two subsequent groups are alike can dearrange in only one manner.

$$C_2H_5NH\text{-}CO\text{-}NHC_2H_5 \rightleftarrows C_2H_5NCO + C_2H_5NH_2$$

If *sym.*-diethylurea is heated with aniline, the gaseous ethylamine which results from the dearrangement escapes and the ethyl isocyanate combines with the less volatile aniline to form *sym.*-ethylphenylurea. This substance can now dearrange into two modes.

$$C_2H_5NH_2 + C_6H_5NCO \rightleftarrows C_2H_5NH\text{-}CO\text{-}NHC_6H_5 \rightleftarrows C_2H_5NCO + C_6H_5NH_2$$

When *sym.*-ethylphenylurea is heated alone at 160°, ethylamine escapes and the phenylisocyanate and aniline combine to form *sym.*-diphenylurea. The urea dearrangement then provides the true explanation of the apparently metathetical reaction in which the ethyl groups of *sym.*-diethylurea are successively replaced by phenyl.[2]

Unsymmetrical disubstituted ureas are obtained in poor yield by refluxing an aqueous solution of urea with the hydrochlorides of secondary amines,[2] and in much better yield by the interaction of secondary amines with nitrourea in aqueous solution at ordinary temperature.[3] They can dearrange in only one manner, namely, to produce cyanic acid and the secondary amine: and their tendency toward dearrangement is so great that they have the odor of the amine even after recrystallization to the highest purity. If *unsym.*-ethylphenylurea is heated for a short time at 150°, the cyanic acid polymerizes to a cyanuric acid which separates from the melt in crystals and the ethylaniline remains in the tube and is readily identified as such.[3] A study of the rate and extent of the dearrangement of a number of *unsym.*-disubstituted ureas is now under way in this laboratory with the expectation that the results will show us the effect of various substituents on the reactivity of molecules in these reversible addition reactions.

The tautomeric substance, cyanamide, is at once a derivative of ammonia and a derivative of cyanic acid; it is ammonia with a cyan group in place of one hydrogen, and it is cyanic acid with NH in place of the oxygen. The formation of dicyandiamide or cyanoguanidine when an aqueous solution of cyanamide is evaporated appears then to be a clear case of urea formation. Dicyandiamide can dearrange in two senses, and when heated above its melting point does indeed yield the expected products, ammonia, cyanamide, and melamine and mellon, the tri-mers respectively of cyanamide and of dicyan*imide*.

$$NH_2\text{-}CN + HNCNH \rightleftarrows NH_2\text{-}C(NH)\text{-}NH\text{-}CN \rightleftarrows$$

polymerizes to melamine $NH_3 + NC\text{-}NH\text{-}CN$ [or NC-NCNH]

polymerizes to mellon

Guanidine dearranges less readily than urea and yields ammonia and cyanamide as would be expected from the familiar method for its synthesis. If it is heated with aniline, the cyanamide shows no tendency to combine with that substance but combines with itself, as it does in the absence of aniline, to form melamine.

A nitro group attached to one of the nitrogen atoms of the substituted urea promotes very greatly the tendency toward dearrangement. Nitrourea dearranges rapidly in water solution at ordinary temperature, and so is readily adaptable for use in synthesis in place of cyanic acid, which is difficult to prepare, and in place of metal cyanates, which contaminate the reaction product with mineral salts. Nitroguanidine dearranges in boiling water or in cold concentrated sulfuric acid solution more readily than guanidine and less readily than nitrourea.

We have been able to show that the dearrangements which are indicated below take place, but have not as yet been able to show that the reactions are reversible. Nor have we as yet any light upon the dearrangement in the other possible manner beyond the fact that both of the substances, heated to decomposition, yield ammonia and amorphous ill-defined residues.

Nitrourea[3] $NH_2\text{-}CO\text{-}NH\text{-}NO_2 \longrightarrow NH_2NO_2 + HNCO$

Nitroguanidine[4] $NH_2\text{-}C(NH)\text{-}NH\text{-}NO_2 \longrightarrow NH_2\text{-}NO_2 + HNCNH$ [or $NH_2\text{—}CN$]

If nitrourea is dissolved in water and the solution is allowed to stand at ordinary temperature for an hour or more, the liquid contains cyanic acid which may be detected by the ordinary method, and it contains another substance which is neither urea nitrate, nor ammonium nitrate, nor nitric acid, for none of these substances yield nitrous oxide on boiling in aqueous solution. The substance yields nitrous oxide when its solution is warmed, and it yields nitric acid when it is subjected to the hydrolytic action of mineral acids.[3] Nitroamide is the only substance which conforms to these specifications. A solution of nitrourea in concentrated sulfuric acid contains no nitric acid, for it yields no nitric acid if heated above the boiling point of that substance, and no ammonium nitrate, but some other substance, necessarily nitroamide, which gives off nitrous oxide on heating and which is convertible into nitric acid in the nitrometer or in the presence of easily nitrated organic substances with which it enters into reaction.[3] Cyanic acid then is found in the dearrangement of nitrourea, and nitroamide, although not isolated, is none the less found by inference and validly demonstrated.

If an aqueous solution of nitrourea is boiled, nitrous oxide escapes and the cyanic acid which is produced escapes in part, polymerizes in part, and in part remains in the aqueous liquid where it may react with various substances which may be introduced. If aniline is added to a saturated

aqueous solution of nitrourea, crystals of phenylurea are deposited[3] after two days standing at ordinary temperature. By the use of other primary and secondary amines, many mono-substituted and unsym.-disubstituted ureas may be obtained in excellent yield.[3] If nitrourea is refluxed with alcohols, carbamic and allophanic esters are produced.[3] A solution of nitrourea in concentrated sulfuric acid is a convenient reagent[3] for the nitration of organic substances which are not injured by contact with sulfuric acid.

When nitroguanidine is dissolved in concentrated sulfuric acid, the solution contains two substances one of which gives off nitrous oxide rapidly on heating while the other gives off carbon dioxide later and more slowly.[4] The first of these substances cannot be ammonium nitrate because ammonium nitrate is converted to nitric acid by the action of one equivalent of concentrated sulfuric acid and therefore would not sustain the action of a large excess of that reagent. It cannot be nitric acid for the solution does not yield nitric acid when it is heated: it yields laughing gas. It cannot be guanidine nitrate for then the carbon dioxide and nitrous oxide would come off simultaneously when the solution is heated. But the substance is convertible to nitric acid, for the solution gives up its NO_2 group quantitatively in the nitrometer and has been found to be a suitable reagent for the nitration[4] of aniline, phenol, etc. The solution therefore contains nitroamide, capable of losing water to form nitrous oxide and capable of combining with water to produce nitric acid. The other substance which is present in a sulfuric acid solution of nitroguanidine, the substance from which the carbon dioxide is produced, might conceivably be guanidine, but, if guanidine were present, nitric acid would be present also. The other possibility is cyanamide. And the production of cyanamide by the dearrangement of nitroguanidine is demonstrated by the fact that an aqueous solution of nitroguanidine boiled with methylamine or aniline yields[4] methylguanidine or phenylguanidine. Although we have not isolated the products, we have thus been able nevertheless to show that nitroguanidine dearranges into nitroamide and cyanamide and have been able to carry out certain syntheses based upon the dearrangement.

To summarize: the mechanism of many reactions in the urea series is the reversible combination of molecules, and all urea derivatives which we have studied dearrange or break down, often in more than one fashion, but always in a predictable manner analogous to that in which urea dearranges into ammonia and cyanic acid. The ease with which various substituted ureas undergo the dearrangement is determined by the nature and position of the substituent groups, and it is expected that a further study of the matter will throw light upon the effect of groups in determining the reactivity of molecules. The products arising from the predictable dearrangement of urea derivatives have been used in synthesis and in some cases have shown themselves to be more convenient for use than other reagents.

[1] Davis and Underwood, *J. Am. Chem. Soc.*, **44**, 2595 (1922).
[2] Davis and Blanchard, *Ibid.*, **45**, 1816 (1923).
[3] Observations not yet published.
[4] Davis and Abrams, not yet published.

AN EQUATION FOR THE HABER EQUILIBRIUM[1]

BY LOUIS J. GILLESPIE

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Read before the Academy November 11, 1924

The equation:

$$\log K_p = (2679.35 + 1.1184\,p)\,1/T - (5.8833 + 0.001232\,p)$$

represents within the experimental error the equilibrium constant values determined by the Fixed Nitrogen Research Laboratory over the temperature range about 325° to 500°C and from 100 atmospheres to the lowest pressures. The equation is serviceable for calculating "K_p" exactly for an equilibrium mixture resulting from the use of a reacting mixture made from atmospheric nitrogen and having a hydrogen-nitrogen ratio equal to 3.24.

The equation:

$$\log K_p = (2172.26 + 1.99082\,p)\,1/T - (5.2405 + 0.0021550\,p)$$

represents well the high pressure data of the same laboratory, but not so many decimal places are serviceable in this case, because the hydrogen-nitrogen ratio is less definitely known.

An attempt to construct one equation for both high and low pressure data fails because of a discontinuity, which is too small to be shown by plotting of isobars, but is strikingly exhibited when the pressure variations of the parameters of the isobars are examined. A similar discontinuity exists between the given data at 30 atmospheres and Haber's data at the same pressure. Both discontinuities are believed to be the result, not of experimental error, but of variation in the composition of the gas mixture.

Evidence is therefore found in the data for the Haber equilibrium that the function K_p is not strictly constant with respect to any variation whatsoever of the internal variables, the number of independent variables being given by the phase rule.

An important experimental task therefore remains; to determine at least around the stoichiometrical composition, the variation of K_p with the composition. At high pressures the maximal yield of ammonia may occur at a hydrogen-nitrogen ratio different from three.

Details of the calculations will shortly be published in the *Journal of*

Mathematics and Physics, vol. 4, no. 2, published by the Massachusetts Institute of Technology.

[1] Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 162.

[Contribution from the Gates Chemical Laboratory, California Institute of Technology, No. 53.]

A CRITICAL POTENTIAL OF METHANE AND ITS ABSORPTION IN THE ULTRA-VIOLET

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In a previous paper[1] it was stated that the maximum in the current potential curve found in a *three*-electrode tube with methane must be due either to a resonance potential of methane or to a large transparency for slow electrons. It was further pointed out that the interpretation of maxima in current-potential curves obtained in *four*-electrode tubes must also take into account the possibility of abnormal transparency at certain velocities. In the meantime Brode[2] has as a matter of fact found a variable mean free path for electrons in methane using the method of Ramsauer,[3] which presumably accounts for the maximum, since it occurs at about the expected velocity. Nevertheless, the whole problem is of such importance that it seemed wise to make a further investigation to see if, in addition to the effect due to transparency, there might not also be a resonance potential occurring in the same neighborhood, accounting for part of the effect. The possibility must also be considered of a critical potential (as distinguished from a resonance potential) at which the molecule assumes a metastable state, without immediate re-emission as in the case of a resonance potential. (The hypothesis of a metastable state has been made before for instance in the case of helium by Franck and Knipping;[4] and, since nothing is known concerning the energy-levels of methane, this possibility must also be considered.)

In this paper experimental work is described which shows that no part of the maximum obtained in three or four-electrode tubes filled with methane can be due to a resonance potential. The work does not eliminate, however, the possibility of a non-radiating critical potential occurring at the voltage in question. The experiments consist in the measurement of the absorption of methane for ultra-violet light and in the study of Lenard photo-electric curves in methane. Before describing them the current-potential curves obtained by the resonance method will be given.

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The Experiments in Four-Electrode Tubes.—The current-potential curves obtained in methane in a four-electrode tube are shown in figure 1. The method of obtaining these curves is fully described by K. T. Compton.[5] A large number of such curves were taken and they all show the maximum. Pressures from 0.2 to 0.9 mm. Hg were used, sometimes a tungsten and sometimes a Pt(CaO) filament being employed. The usual interpretation of such curves would ascribe the maximum to a resonance potential at about five volts (corrected for initial velocity). However, these curves did not show a second maximum at about 10 volts, as might have been expected from the conditions of experiment and from analogy with similar curves in mercury and other substances.[6] This lead to the belief that the maximum was not due to a resonance-point, but to large transparency for slow electrons.

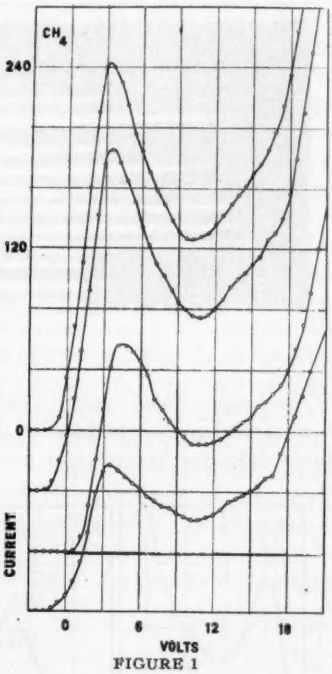

FIGURE 1

If it were possible to get spectroscopic data for methane, this question could easily be decided; for methane should show a line or band spectrum in the region of 5 volts or 2400Å. The reason that no spectroscopic data exist is that the substance decomposes under the conditions maintained in an ordinary discharge tube. However, absorption measurements are of course possible; and, in coöperation with Dr. Richard M. Badger of this laboratory, they have been carried out as described below.

The Absorption of Methane for Ultra-Violet Light.—The light from an aluminum spark under water was sent through a layer of methane 54 cm. long into a Hilger quartz spectrometer, for the use of which we wish to thank Prof. R. A. Millikan. The gas was at atmospheric pressure. Figure 2 shows that no absorption could be detected in the region around 2400Å. For comparison benzene at 0.13 atmosphere was placed in the tube, and its absorption was easily shown. Although it may be argued that a thicker layer of methane or the gas at higher pressure might show absorption, yet it is felt that the conditions were stringent enough to make it very improbable that absorption exists. If it be admitted that the experiment indicates *no* absorption in the ultra-violet region, then methane has no

radiation potential at five volts. Additional proof of the correctness of this inference is afforded by the following Lenard experiments.

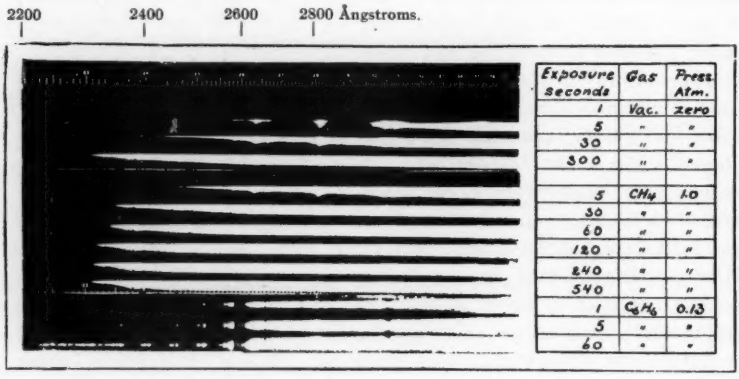

FIGURE 2

The Lenard Photo-Electric Experiments in Methane.—These experiments were carried out on the basis of the following considerations. If methane has a radiation potential at five volts, the light of wave-length 2400Å. should liberate photoelectrons from the platinum receiving plate, and a photo-current beginning at five volts should be detected in analogy with the same type of experiment in mercury by Franck and Einsporn,[7] and in nitrogen by Brandt.[8] However, the curves in figure 3 A show that no positive current is detected below 17 volts, and this is undoubtedly due not to electrons, but to positive ions reaching the plate, as may be judged in the usual way from the magnitude of this current. From the very pronounced maximum in the resonance curve it would be expected that enough photo-electrons would be liberated from the plate at five volts to be detected; especially since

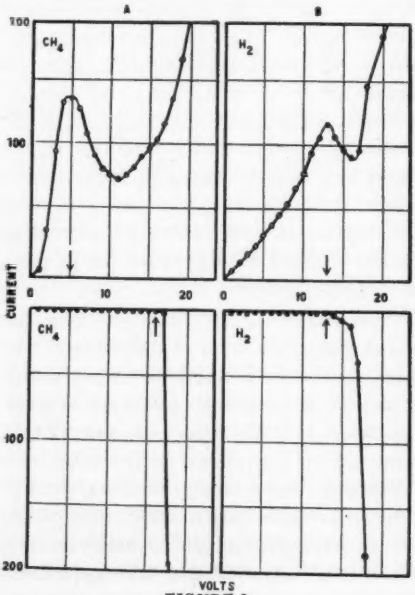

FIGURE 3

similar experiments in hydrogen showed that the photo-electric curves (shown in figure 3 B) start at 13 volts—the same voltage at which the maximum in the resonance curve appears.

Conclusions.—These experiments, it is believed, prove that five volts is not a resonance potential of methane. But it cannot be argued that the maximum is due solely to transparency for slow electrons, if we draw, as is customary, a distinction between a resonance and a critical potential of a gas. At the *resonance potential* the impinging electron excites the atom or molecule which gives out radiation on subsequent return to normal. At a *critical potential* the impinging electron brings the atom or molecule into a metastable state from which the system may reach its normal state without necessarily giving out its energy as radiation, but returning perhaps by some sort of impact of the second kind. If we make this hypothesis, the maximum under discussion may in part be due to such a critical potential for in that case the absorption results and the Lenard curves would be as found.

Summarizing the results of these experiments and the earlier ones in three-electrode tubes it may be said that a maximum in the current may be due to the following causes: (1) a true resonance potential of the gas; (2) a possible critical potential; (3) variable mean free path of the electron; (4) dissociation of the molecule; (5) thermal decomposition by the hot filament. In particular it is to be pointed out that critical potentials obtained by the resonance method are not easily interpreted for a substance for which no spectroscopic data exist.

It is a pleasure to thank Professor Richard C. Tolman for suggestions received.

[1] G. Glockler, *Proc. Nat. Acad. Sci.*, **10**, 155 (1924).
[2] *Physic. Rev.*, **23**, 664 (1924).
[3] *Ann. Physik*, **64**, 513 (1921).
[4] *Zt. Physik.*, **1**, 320 (1920).
[5] Critical Potentials, *Bull. Nat. Res. Council No.* **48**, vol. 9, pt. 1, page 9.
[6] *Ibid.*, pages 8 and 19.
[7] *Zt. Physik.*, **2**, 18 (1920).
[8] *Ibid.*, **8**, 32 (1921).

STUDIES IN CATALYSIS

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Frequently the term catalysis is associated with important processes such as the fixation of atmospheric nitrogen, hydrogenation or "hardening" of vegetable oils, vulcanization of rubber, manufacture of Bakelite, and many other operations of a similar nature. Usually the function of a catalytic agent is to initiate reactions or to accelerate those which without this aid would proceed too slowly to be of value.

At present considerable attention is being given to another sort of catalysis. It has been known for sometime that the rate of decomposition of unstable materials like smokeless powder and hydrogen peroxide can be greatly decreased by the addition of a small amount of compounds known as stabilizers or negative catalysts. The writer has recently studied problems of this general type in detail with the hope of establishing the mechanism of negative catalysis and of ascertaining principles which might be of general use in choosing inhibitors or stabilizers.

When chloroform is exposed to light, even in stoppered bottles of ordinary glass, it gradually develops an acid reaction and acquires some properties of an oxidizing agent. Compounds found in chloroform which has undergone decomposition are phosgene, hydrogen chloride and chlorine. Probably the reactions involved are as follows: $H C Cl_3 + O_2(air) = HCl + Cl_2 = C\begin{matrix}O\\|\\O\end{matrix}$;

$2\ Cl_2 = C\begin{matrix}O\\|\\O\end{matrix} = 2\ Cl_2\ CO + O_2$. Obviously these substances render chloroform unfit for use as an anaesthetic. It is customary to add a small amount of ethyl alcohol to chloroform to minimize the changes which have been mentioned. The decomposition of chloroform has received attention from many investigators. Results obtained have been explained by saying that stabilizers reacted with the products of decomposition. On this basis one would expect that only materials easily oxidized or chlorinated would be effective as inhibitors. There are several serious objections to this point of view, including the fact that very small amounts of preservatives are sufficient for large quantities of chloroform.

A short time ago a theory was put forward by Taylor in which it was stated that, in certain cases at least, the so-called inhibitors function by formation of molecular compounds with the active molecules of the substance being preserved. On this basis inhibitors are true negative catalysts

and not reagents. *This idea has been the guiding principle in our work.* In the case of chloroform one would say that the chloroform molecules have a greater affinity for the stabilizer than for the oxygen of the air. Since molecular compounds are very loose combinations which are formed and decomposed extremely rapidly, a comparatively small quantity of stabilizer is able to care for large quantities of chloroform.

We have repeated some early and recent experimental work and have investigated many stabilizers not previously studied. There seems to be a remarkable parallel between molecular compound formation and negative catalysis. Substances such as ethyl ether, phenol, resorcinol and benzene are stabilizers for chloroform. Evidence of molecular compound formation is available for each of these compounds. It seems unlikely that benzene would be oxidized by decomposed chloroform. Also we have been unable to find any conclusive evidence of chlorination of these four preservatives. On the other hand, carbon tetrachloride is not useful as a negative catalyst. One would not expect this material to form a molecular compound with chloroform. Of course the evidence regarding some of the substances investigated cannot be so readily interpreted as the facts we have just mentioned. In the limited time available it is not possible to give many details, but the writer is prepared to say that in dealing with more than twenty-five compounds, including amylene, benzene, *m*-xylene, toluene, naphthalene, liquid petrolatum, nitrobenzene, *p*-nitrotoluene, *m*-dinitrobenzene, methyl alcohol, ethyl alcohol, phenol, resorcinol, α-naphthol β-naphthol, pyrogallol, ethyl ether, diamyl ether, phenetole, carbon tetrachloride, acetic acid, cinnamic acid, benzidine and dianisidine, no really serious contradiction of his thesis has been found.

In the prevention of the fading of dyes we have another field in which inhibitors can be employed. Apparently in certain cases loss of color on exposure to light is due to oxidation. One might expect that some of the compounds which retard the decomposition of chloroform would also increase the fastness of certain coloring matters to light. Skeins of cotton and wool were dyed with representative colors of the azo, basic and acid types. In every case investigated it has been found that the fugitive dyes could be more or less protected against the action of light by treatment of the dyed wool or cotton with a dilute solution of phenol or of resorcinol. A piece of yarn colored with malachite green faded a great deal after one week of exposure to light; no color change was apparent in one month, after treatment with resorcinol solution. Among the thirty colors investigated were also shades of blue, yellow, orange, brown and black. It seems advisable to attempt utilizing the information obtained, by synthesizing dyes of molecular structure such that there would be present groups similar to those found in stabilizers. By a rather indirect use of this idea we have succeeded in obtaining from primuline, which usually is described as yield-

ing somewhat fugitive developed colors, a series of brilliant azo dyes very fast to light.

Although the work mentioned in this paper deals with only a small part of the subject the evidence which has been secured indicates that the idea of molecular compound formation should be thoroughly tested. Since the organic chemist specializes in problems connected with molecular structure and the residual affinity of atoms or groups he may find this theory useful in the choice of negative catalysts for many purposes.

ON THE MEASUREMENT OF CRITICAL THERMAL INCREMENT FOR BIOLOGICAL PROCESSES

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The attempt to classify biological activities upon the basis of their velocities as affected by temperature[1] involves for a number of cases the adjustment of curves to data inevitably subject to several sources of variation. One of these arises from the fact that the measurements may be secured with different individuals at each of several temperatures. The latitude of variation in series of data obtained in this way may be large, and unless great numbers of observations are available interpretation may be difficult.[2] Indication already obtained as to the theoretical significance of the exact quantitative relationship between velocity of a vital process and temperature make it desirable to demonstrate the limits of variation in material which is as nearly as possible biologically homogeneous.

An illustration is provided by the frequency of the heart-beat in the silkworm. Larvae were bred from eggs given by Dr. R. W. Glaser. The caterpillars used came from eggs laid by one female; this fact, coupled with the highly inbred character of these animals, insures exceptional genetic uniformity. The heart-beat was counted for each of a number of individuals of the same age, reared throughout under identical conditions.[3] The details of these experiments well be described in another place. It is sufficient here to state that a larva when under observation was motionless and quietly feeding on a mulberry leaf, in a closed glass chamber immersed in water. The temperature was obtained with a thermometer reading to 0.01°C. We shall deal merely with the temperature affect above 15°C. Below this temperature, complications ensue and there occur changesw hich are only slowly reversible. It is significant that 15° is in this instance as

in so many others, [1,4] a "critical temperature" for organic phenomena; not only is the heart beat abruptly affected in a special manner by exposure to temperatures even slightly below 15°, but the larva promptly ceases to feed.

Observations made upon several individuals are plotted in Figure 1. The control of heart-beat frequently by temperature is adequately expressed in the equation

$$\frac{Frequency_2}{Frequency_1} = e^{\frac{\mu}{2}\left(\frac{1}{T}-\frac{1}{T_1}\right)}$$

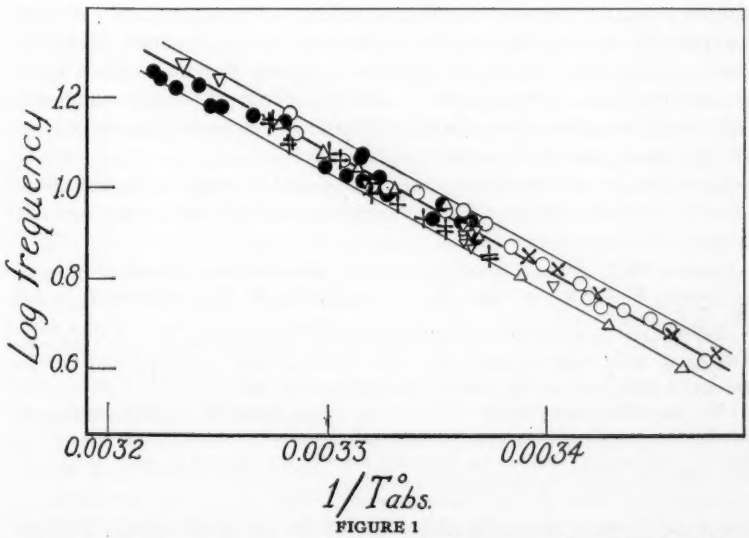

FIGURE 1

The relation between temperature (15° to 38°) and frequency of heart beat in *Bombyx* larvae. Each point is the mean of a series of closely concordant measurements. The several individuals (6) are represented by different symbols. The latitude of variation in heart beat at constant temperature is a constant fraction of the mean frequency for that temperature. This rule holds for a single individual and also for the observations made with different larvae similar in genetic and environmental history, though the degree of variation is probably not identical in all individuals.

as evidenced by the linear relation of *log frequency* to *reciprocal of absolute temperature*. The plotted points are each the mean of a series of determinations; in every case the degree of variation in a single series is very slight, in fact less than the diameter of the symbol. Therefore such variation is is evidenced is real variation. But it is clear that the individually determined points are sharply confined to a band centered upon the best-fitting line. The latitude of variation in frequency is at any temperature a fixed

fraction of the corresponding mean frequency. For the different individuals the amount of deviation is about the same.

The critical termal increment, μ, is in this case 12,200 calories. This agrees quantitatively with the increment for a number of other activities among arthropods[1] in which "nerve center" activity may be presumed to be the determining phenomenon.

Our purpose now, however, is not to dwell upon the meaning of the specific increment for heart rhythm, but to present the fact that when sources of variation are reduced to a reasonable minimum the velocities of biological phenomena are found to obey with exactitude the law of temperature influence upon irreversible chemical processes. The nature of the residual variations in velocity (frequently), as disclosed in this and other instances,[2] makes it important for precise analysis to secure numerous observations at close intervals of temperature.[5] Careful analysis of this type applied to representative cases makes it possible to interpret instances unavoidably involving more influential sources of variation.

A detailed discussion of the experiments, and a comparative account of thermal control of heart rhythm in various animals, will appear in *The Journal of General Physiology*.

[1] Crozier, W. J., *J. Gen. Physiol.*, **7** (123, 189); these PROCEEDINGS, **10** (461).

[2] Crozier, W. J., and Federighi, H., *J. Gen. Physiol.*, **7** (151); Crozier, W. J., and Pilz, G. F., *Ibid.* **6** (711).

[3] We are glad to thank Mr. L. R. Campbell for his assistance in caring for the larvae.

[4] Crozier, W. J., and Federighi, H., *Proc. Soc. Exp. Biol. Med.*, **21** (56); *J. Gen. Physiol.*, **7** (151); Glaser, O., *Ibid.*; *J. Gen. Physiol.*, **7** (177).

[5] The reasoning underlying the biological use of the Arrhenius equation for reaction velocities as function of temperature should warn against "averaging" observations from different individuals. Failure to avoid this practice has resulted in some curious errors in the literature of "temperature coefficients."

MICROCHEMICAL COLOR REACTIONS AS AN AID TO THE IDENTIFICATION AND CLASSIFICATION OF BRAIN TUMORS

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Cellular differentiation during embryological development in the last analysis is probably the result of chemical differentiation in the protoplasm of the cells. The nature of these differences is very obscure. We know in a general way that synthetic processes in the cells are condensations with dehydration, but the reasons for these processes resulting in a certain product in one cell, an entirely different product in another, and the steps through which the different results are achieved are but dimly surmised.

But certain it is that cells elaborate very different substances by means of which they may be recognized under the microscope. Sometimes these substances are retained within the cell, as in the case of the Nissl bodies of the nerve cells. Sometimes they are discharged to the exterior, as in the case of the externally secreting cells of the stomach and other glands. Again, these substances may be expelled into the intercellular spaces, as is the case with the collagen and mucin formed by the connective tissue cells.

The chemical constitution of these substances elaborated by the various cells is often unknown, but they may be made to give certain chemical or physicochemical reactions resulting in color changes. If such a color change is produced by but one substance, elaborated by a certain cell, this color change is of the greatest value in identifying that substance even though its chemical constitution is unknown, and secondarily is of value for the identification of the cell which elaborates it. The search for such specific color reactions constitutes a large body of microscopic research, for such a change renders the substance visible under the microscope, making it stand out in contrast to the surrounding tissue elements.

The application of these microchemical color reactions to the study of tumors lies in the fact that the terminology of tumors is based on that of the normal cells from which the tumor cells arise, or on that of the normal cells which they most resemble in their differentiation. An attempt is therefore made to identify the tumor cells by means of the substances which they elaborate, such as collagenic fibrils, neuroglia fibrils, etc., and the tumor is named accordingly.

There are, however, tumor cells which elaborate no special substances by which they may be recognized. Consequently, the identity of these cells is often most obscure. There is, however, another possible and promising method of identification. If different cells elaborate substances of very different character, it is reasonable to suppose that there may also be a difference in the chemical constitution of the protoplasm of the various cells from which these various substances are elaborated. It would doubtless be a smaller difference than that between the specialized elaboration products, but nevertheless possibly sufficient to give differential reactions similar to those obtained with the products of elaboration themselves.

Such, in fact, is the case with the various types of cells in the central nervous system. It has long been known that such a specific reaction may be obtained with the cytoplasm of the nerve cells, but it remained for Ramon y Cajal and his pupils to show that three other distinct types of cells giving similar specific reactions existed in the interstitial or supporting tissues. These types are known as the neuroglia, the microglia and the oligodendroglia.

Practically all of the true tumors of the central nervous system are com-

posed of these supporting elements rather than of the nervous tissue itself. The neuroglia cells have long been recognized in these tumors by means of the fibrillae which they usually elaborate, known as neuroglia fibrillae, but many tumors are encountered in which no neuroglia fibrillae can be found and the nature of their cells has long been disputed.

The origin of many at least of these doubtful tumors may be established by means of specific physico-chemical reactions of the cytoplasm of their cells. This is particularly true of the common tumors of the neuroglia in which the tumor cells have not elaborated fibrillae (spongioblastomas). Some evidence has also been obtained to show that the microglia and the oligodendroglia form cerebral tumors as well.

VIRUS ENCEPHALITIS IN THE RABBIT

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Under the designation of virus encephalitis may be grouped a form of inflammation of the brain in the rabbit induced by the inoculation of the contents of febrile herpes esicles and certain other but allied substances derived from man.

Among the substances which have been successfully employed for producing virus encephalitis in the rabbit are certain materials, of diverse origin, taken from cases of epidemic (lethargic) encephalitis. These materials include the secretions of the nose and throat, filtered through earthenware filters to remove ordinary bacteria, extracts of the nasopharyngeal mucosa, removed at autopsy and freed from bacteria in the same manner, fragments of the brain, taken at autopsy, and cerebrospinal fluid, collected by lumbar puncture during life.

At the outset and for several years, until recently, the condition which we propose to call "virus encephalitis in the rabbit" was believed to differ etiologically, according as it was incited by the hypothetical virus of epidemic encephalitis, or the recognized virus of herpes. The virus encephalitis of the rabbit arising from epidemic encephalitis in man was first studied extensively. It was not until the corresponding condition of febrile herpes was equally minutely studied that the similarity of the two processes became evident. This resemblance is so exact and complete that, with few exceptions, students of the subject have come to believe the two processes as identical.

The confusion which persisted over a period of several years arose not

only from imperfection of knowledge relating to the properties of the substances carried by inoculation from man to the rabbit, but also from lack of knowledge of pathological states in the brain of the rabbit present before the inoculations were made. In other words, account was not taken of the occasional and sometimes wide prevalence of encephalitis due to parasitic invasion of the brain by organisms of rabbit origin, to which the name of "preinoculation encephalitis" is applicable. This latter inflammation of the brain may reach severe proportions without arousing noticeable symptoms of disease. When, therefore, animals thus affected succumb from any cause, the evidences of encephalitis are found and may therefore be ascribed falsely to the inoculation performed. That this mistake has been made in not a few instances may now be regarded as certain.

The confusion is accounted for also by the imperfection of our knowledge of the properties and especially of the distribution of the herpes virus in man. Febrile or ordinary herpes has hitherto been regarded as a mild, local affection of annoying character, but small significance. It has long been known that certain persons are very subject to its appearance, especially about the lips, and suffer attacks from minor and miscellaneous causes: colds, indigestion, certain foods and drugs, and still other incidents are followed by the eruptions. But nothing was, or very well could be known, of a wide occurrence of the provoking agent of the eruptions, a virus, before the remarkable susceptibility of the rabbit to its inoculation was discovered.

We have now learned that, although the rabbit does not naturally suffer from infection with the virus of febrile herpes, the implantation, in diverse ways, of the contents of the vesicles on this species leads to severe effects in part counterparting those occurring in man, in part far more severe in that the brain becomes affected and usually with the result of a fatal outcome. When the virus-containing materials are implanted in the eye of the rabbit, inflammation and vesiculation of the cornea arise; when in the skin, inflammation and vesiculation of that structure appear; when in the brain, fatal encephalitis follows. Not infrequently also the corneal and skin infections, instead of remaining local and healing, as in man, extend to the brain and induce a fatal encephalitis—an effect unknown in human pathology.

The inoculation into rabbits of materials from many other human sources has led, in occasional instances, to the appearance of an indistinguishable variety of encephalitis, thus indicating that the materials carried a virus of the nature of the herpes virus. This is the probable explanation of the instances of successful infection of the rabbit with so-called virus of encephalitis. Among the materials active in this way is the cerebrospinal fluid, from which it is to be inferred that the herpes virus receives at times a general distribution throughout the human body, passing, when that hap-

pens into the cerebrospinal fluid, where its presence is disclosed by the rabbit inoculation—the only method now available for the purpose.

In this way we have demonstrated the virus of herpes in the cerebrospinal fluid taken from a case of syphilis of the central nervous system. In this way, also, are explained, probably, the few successful attempts as well as many failures to discover the virus in specimens of cerebrospinal fluid taken from cases of epidemic encephalitis.

If we turn now from the effects of the inoculation of the virus of herpes from man to the rabbit and consider the effects of the passage of the virus from rabbit to rabbit, which is readily achieved, we uncover certain interesting facts. As would be expected, the severest examples of inoculation encephalitis are those which follow the intracranial injection of brain tissue carrying the virus. The severity in this instance refers to the rapidity of the onset of symptoms and the intensity of the inflammatory reaction. Filtrates, through Berkefeld candles, of such suspensions produce effects somewhat slower in appearance, but equally fatal, while the inflammatory response is milder. When the brain is invaded from skin or cornea, after inoculation, the disease incubation period may be still longer and the inflammation still milder, although the fatal effects may be as numerous. These differences are accounted for, in part certainly, by the directly injurious action of the inoculated materials, greatest in the case of the tissue suspension, upon the delicate and sensitive brain structures.

The variation in degree of inflammatory appearances and severity of symptoms becomes, under these circumstances, a matter of interest and speculation. From what has been stated already about the preinoculation encephalitis of the rabbit, it follows that even much cellular infiltration about blood vessels and in brain tissue can occur independently of striking symptoms of disease. In the same manner wide disparity exists between the detectable microscopic brain lesions in virus encephalitis in the rabbit in instances of fatal outcome. Once the effects of the preinoculation encephalitis are excluded it becomes evident that severe symptoms and death may ensue with few detectable lesions in the brain. The conclusion to which this fact, if fact it be, points is that the virus attacks nerve cells directly affecting them in various ways, sometimes merely stimulating them to over activity (hence certain symptoms), sometimes destroying them (hence other symptoms). This probable direct action of the virus upon the nerve cells, as distinguished from the effects of inflammatory outpourings of fluids and cells, has been little studied.

Although the brain tissue of the rabbit may be richly charged with the virus, yet the cerebrospinal fluid may be free of demonstrable amounts. This is an interesting and perhaps unexpected finding. It recalls the corresponding fact in poliomyelitis in man and in the monkey. On the other hand, the virus has been shown to be present in the urine of infected

rabbits. Obviously it may, under certain conditions, pass the kidney barrier from which it must be supposed to circulate with the blood. No one has, as far as I know, detected the virus in the urine in man. I am not aware that it has even been searched for there. Although certain Italian investigators report having demonstrated it in blood taken from persons suffering from febrile herpes, the experiments, as reported, arouse distrust. But the finding of the virus, if rarely, in the cerebrospinal fluid of man and also, if very exceptionally, in the rabbit, and in the urine of the rabbit may be taken to show an occasional, at least, general or blood distribution of herpes virus in both species. Although the rabbit reacts to the presence of the virus in the blood with symptoms of severe encephalitis, the human being is not known to suffer in any degree from this source. Other rodents—guinea-pig, rat, mouse—respond with fatal encephalitis to intracranial but not to intravenous injection of the virus, while birds and other mammals—monkey, dog, cat—are unaffected even by direct inoculation of the virus into the brain tissues.

NOTES ON STELLAR STATISTICS. II: THE MATHEMATICAL EXPRESSION OF THE LAW OF TANGENTIAL VELOCITIES

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Of the velocity laws used in recent years, the form proposed by Schwarzchild, i.e., a normal error function in the logarithms of the velocities, has met with considerable success. Subsequently it has become necessary to make the geometric mean velocity in this law a function of the absolute magnitude. In view of the difficulty of grasping the physical significance of such a logarithmic law, it is well to bear in mind that this law is only a rough statistical description of the celestial phenomena. If the approximation is not carried too far the logarithmic law suffices to represent space as well as tangential velocities and total as well as corrected velocities. With more numerous and more accurate data it has been thought necesary in some quarters to apply slight modifications to the logarithmic law. The advantage gained in representation, however, is not enough to outweigh the greater difficulty in physical interpretation. On the other hand the suggestions of a limiting velocity or a "velocity restriction" have emphasized again the importance of the Maxwellian law.

It appears advantageous to follow the original suggestion made by Kapteyn and others to assume a limited number of Maxwellian functions. In

accordance with the views stated above the simplest assumption that can be made appears to be that of a finite number of isotropic distributions on each of which a drift is superposed. The first problem is to obtain the frequency function of the observed tangential velocities and for this it will be enough to treat but one of these Maxwell functions.

If h is the constant of this distribution, V the speed of the drift, and λ the angular distance between á certain infinitesimal area in the sky and the apex of the drift, we have the following expressions for the distributions of velocities directed toward the apex and of velocities at right angles to this direction:

$$f(v)dv = \frac{h}{\sqrt{\pi}} \exp.[-h^2(v - v_0)^2]dv, \qquad f(\tau)d\tau = \frac{h}{\sqrt{\pi}} \exp.[-h^2\tau^2]d\tau. \quad (1)$$

Introducing the total tangential velocity T by:

$$v = T\sin\theta, \qquad \tau = T\cos\theta \quad (2)$$

the frequency function of linear tangential velocities for all stars in the sky follows:

$$\Psi(T)dT = TdT \int_0^{\pi} d\lambda \int_{-\pi/2}^{\pi/2} d\theta \frac{2h^2}{\pi} \exp.[-h^2(T^2 + V^2\sin^2\lambda - 2TV\sin\lambda\sin\theta)]\sin\lambda \quad (3)$$

or:

$$\Psi(T)TdT = TdT \int_0^{\pi} \frac{2h^2}{\pi} \exp.[-h^2(T^2 + V^2\sin^2\lambda)]\sin\lambda d\lambda \int_{-\pi/2}^{\pi/2} \exp.[2h^2TV\sin\lambda\sin\theta].d\theta$$

The second integral is of the form:

$$F(x) = \int_{-\pi/2}^{\pi/2} \exp.(x\sin\theta).d\theta \quad (4)$$

Comparing this with the definite integral expressing the Bessel function, or, still easier, differentiating equation (4) twice and writing

$$\frac{\partial^2 F}{\partial x^2} = F(x) - \frac{1}{x}\frac{\partial F}{\partial x}$$

we see that the solution of (4) is given by

$$F(x) = \pi J_0(ix) = \pi J_0(2h^2VT\sin\theta\sqrt{-1})$$

We then have:

$$\Psi(T)dT = TdT \int_0^{\pi} 2h^2 \exp.[-h^2(T^2 + V^2\sin^2\lambda)]. J_0(2h^2VT\sin\sqrt{-1}).\sin\lambda d\lambda.$$

$$= TdT \int_0^\pi 2h^2 \exp.[-h^2(T^2 + V^2 \sin^2\lambda)]. \sum_0^\infty \frac{(h^2VT)^{2j}}{(j!)^2} . \sin^{2j+1}\lambda d\lambda.$$

Writing $\cos\lambda = u$, this transforms into:

$$\Psi(T)dT = TdT \int_0^1 2h^2 \exp.[-h^2(T^2 + V^2 - V^2u^2)]. \sum_0^\infty \frac{(h^2VT)^{2j}}{(j!)^2} .(1 - u^2)^j du.$$

In performing the integration it appears advantageous to put:

$$a = h^2V^2, \qquad z = hT$$

Repeatedly integrating by parts and expanding into power series we obtain for the final answer:

$$\Psi(T)dT = 2h^2e^{-h^2(T^2+V^2)}\, TdT. \sum_0^\infty A_j z^{2j}. \tag{5}$$

$$A_j = \frac{2^j a^j}{j!}\left[\frac{1}{1.3.5.7\ldots(2j+1).0!} + \frac{a}{3.5\ldots(2j+3).1!} + \frac{a^2}{5.7\ldots(2j+5).2!} + \ldots\right]$$

These final expressions contain T and V only in the combinations hT and hV, accordingly, since h is connected with the mean peculiar velocity w by the equation $h = 1/w\sqrt{\pi}$, $\Psi(T)$ gives us in explicit form the frequency function of the ratio between the tangential and the mean peculiar velocity, and contains only one parameter, the ratio between the drift velocity and the mean peculiar velocity.

Using z and a exclusively in the right hand side of equation (5) we obtain: $\Psi(T)dT = 2e^{-z^2} zdz \sum_0^\infty A_j e^{-a} z^{2j}$ or: $\Psi(T)dT = 2e^{-z^2} zdz \sum_0^\infty e^{-a} a^j C_j z^{2j}$

In most instances we have to deal with values of a less than 1.27 (corresponding to $V = 2w$) in which case the series expressions derived for the coefficients A_j converge very rapidly. The term a^j makes the A_j very sensitive to small changes in a, accordingly it is desirable to leave this factor out, and to tabulate, not A_j, but $C_j = A_j/a^j$, as a function of a, a procedure which will facilitate interpolation considerably.

Table I gives the values of the first seven coefficients C_j for values of V/w between 0 and 2. The value $V/w = \sqrt{\pi} = 1.7724$, is inserted, since for this particular value, $a = 1$, and the power series take on their simplest form. The tenth column gives the values of e^{-a}; with these, and the val-

ues for a shown in the second column, the coefficients of z^j may be easily computed for any specific value of V/w.

The coefficients A_j satisfy the condition $\sum_0^\infty A_j\, j! = e^a$, necessary, in order that $\Psi(T)$ may be a true frequency function, and $\int_0^\infty \Psi(T)dT = 1$.

Having once obtained $\Psi(T)$ we can now calculate the arithmetic mean tangential velocity T_a, which will be purely a function of $a = V^2/\pi w^2$. We have:

$$T_a = \int_0^\infty T.\Psi(T)dT = \frac{1}{h}\int_0^\infty 2e^{-z^2}z^2dz.\sum_0^\infty A_j e^{-a}z^j.$$

Integration gives:

$$T_a = \frac{\sqrt{\pi}}{2h}\left[1 + \frac{a}{1.3} - \frac{a^2}{3.5.2!} + \frac{a^3}{5.7.3!} - \frac{a^4}{7.9.4!} + \ldots\ldots\right]$$

The values of T_a, expressed in terms of the mean value T_o, when $a = O$ ($T_o = \sqrt{\pi}/2h$), are entered in the last column of Table I for different values in the argument a. In a subsequent paper we shall derive a similar expression for the uncorrected radial velocity R_a; and we shall then be able to make an immediate comparison between crude proper motions and crude radial velocities.

TABLE I

V/w	a	C_0	C_1	C_2	$C_3.10$	$C_4.10^3$	$C_5.10^4$	$C_6.10^{16}$	e^{-a}	T_a/T_o
0.000	0.0000	1.000	0.667	0.133	0.127	0.705	0.256	0.658	1.0000	1.000
0.50	0.0796	1.027	0.678	0.135	0.128	0.711	0.258	0.661	0.9235	1.026
0.75	0.1791	1.058	0.684	0.136	0.129	0.717	0.260	0.665	0.8361	1.055
1.00	0.3183	1.117	0.712	0.138	0.132	0.727	0.263	0.672	0.7274	1.10
1.25	0.4974	1.195	0.745	0.143	0.135	0.739	0.267	0.680	0.6082	1.15
1.50	0.7164	1.308	0.784	0.148	0.138	0.756	0.272	0.692	0.4886	1.22
1.75	0.9748	1.454	0.832	0.156	0.143	0.776	0.278	0.705	0.3773	1.30
1.772	1.0000	1.463	0.835	0.156	0.143	0.778	0.278	0.706	0.3682	1.31
2.00	1.273	1.653	0.896	0.164	0.149	0.801	0.285	0.721	0.2799	1.38

ECONOMICS AND THE CALCULUS OF VARIATIONS

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1. The writer is not the first to venture to state a general theory in mathematical terms of a subject which is not unfairly regarded as compounded somewhat indefinitely of psychology, ethics and chance. Being more than a mere mixture, however, it is equally fair to say that a separate analysis may apply; indeed, in economics we are interested in the body of laws or de-

ductions which may be inferred from convenient or arbitrary economic hypotheses, however, they may be founded—in fact, fiction, statistics, habits or morals—what we will. This process of inference, if it is worthy of the effort, may be made mathematical. And a general theory, besides whatever merit it may have in the classification of phenomena, at the same time does suggest both particular problems and methods for their study.

Since our task is to discuss the flow of commodities or services through the various compartments into which an economic system may conveniently be subdivided let these compartments be numbered $1, 2, \ldots n$, and let $\dot{x}_i$ be the rate at which the specific commodity or service i is produced in its compartment $[i]$. Let $\dot{X}_i$ be the rate at which this commodity issues from $[i]$, $r_i(t)$ the amount of it which is present at time t in $[i]$, and $\dot{r}_i = dr_i/dt$. A compartment may consist of the services of many individuals, e.g., manual labor in a certain place; or the individual may at the same time figure in several different compartments, e.g., with labor in one and with some form of capital in another. We have

$$\dot{x}_i - \dot{X}_i = \dot{r}_i \tag{1}$$

With regard to exchanges among the compartments, let $\dot{x}_i^{(j)}$ be the rate at which the commodity or service i is transferred from $[i]$ to another compartment $[j]$, and $\dot{r}_i^{(j)}$ the portion of this which is not used in the production of the commodity or service j. We have then

$$\dot{X}_i = \sum_{j=1}^{n} x_i^{(j)} \tag{2}$$

Further let $\varphi_k \overset{\infty}{\underset{t}{[}}\dot{x}_1, \ldots]$, $k = 1, 2, \ldots m$, and $\pi_\rho \overset{t_2}{\underset{t_1}{[}}\dot{x}_1, \ldots]$, $\rho = 1, 2, \ldots \sigma$, be functionals which we may call, respectively, functionals of manufacture (in the nature of cooking recipes), and characteristic functionals whose extremal positions will determine the variable functions of the system (say, one or more integrals with respect to t of weighted sums of squares of rates of production, or various total profits over an interval of time, or—sinister suggestion—the total profit for some privileged set of compartments, or some convenient sociological character). These functionals may involve as arguments any quantities of the system, over the intervals of time specified.

A general system of economics may now be regarded as given by the following equations

$$\varphi_k \overset{\infty}{\underset{t}{[}}\dot{x}_1, \ldots] = 0, \; k = 1, 2, \ldots, m, \tag{3}$$

$$\delta_{\dot{x}_{\rho_1}} \ldots \pi_\rho \overset{t_2}{\underset{t_1}{[}}\dot{x}_1, \ldots] = 0, \; \rho = 1, 2, \ldots, \sigma, \tag{4}$$

where the subscripts of the variation sign indicate the quantities which

are allowed to vary, no two sets having any common members for different values of ρ. The presence of more than one characteristic function for one economic system indicates a competitive character for that system.

From the nature of $[i]$ it may happen that $\dot{x}_i^{(i)} = 0$, so that in (2), Σ may be replaced by Σ'. For most compartments it may be convenient to regard the $\varphi_k = 0$ as solvable for the various $\dot{x}_i^{(j)}$ in the form

$$\dot{x}_i^{(j)} - \dot{r}_i^{(j)} = \int_i^\infty \dot{x}_j(\tau)\, d_\tau f_i^{(j)}[\dot{x}_1, \ldots | \tau], \tag{3'}$$

where, if the solution is linear in $\dot{x}_j$, according to some law of proportionality the $f_i^{(j)}$ will not involve $\dot{x}_j$, and where often $f_i^{(i)} \equiv 0$. Usually also the π_ρ will be additive with respect to intervals of time so that (4) may be rewritten:

$$\delta \dot{x}_{\rho_1} \ldots \int_{t_1}^{t_2} F[\dot{x}_1 \ldots | \tau]\, d\tau = 0, \tag{4'}$$

and the typical problem will be one where only initial values of certain of the variable quantities will be given.

2. Fundamental for most economic systems is the analysis of the compartments relating to money. For simplicity, let us consider these as a single one, the first, not distinguishing currency and bank deposits subject to check, or banks or mints of various accessibilities. The equations (1) to (3) which involve 1 as suffix or index will serve incidentally to define certain ratios, $p_1, \ldots p_n$ called prices. Thus we have

$$\dot{x}_1 - \dot{r}_1 = \dot{X}_1 = \sum_{k=1}^{n} \dot{x}_1^{(k)}$$

$$\dot{x}_1^{(k)} = \dot{r}_1^{(k)} + \sum_{i=1}^{n} p_i \dot{x}_i^{(k)} = p_k \dot{x}_k + \dot{E}_k'$$

where $\dot{E}_k'$ is the flow of credit into $[k]$, and the last member of the equation results from eliminating the equations for credit. Of course the rate of payment of loans as they are due appears as one of the items of the middle member, which is made more explicit in the equation

$$\dot{x}_1^{(k)} = \dot{r}_1^{(k)} + \sum_{i=1}^{n}{}' p_i \left\{ \dot{r}_i^{(k)} + \int_i^\infty \dot{x}_k(\tau) df_i^{(k)} \right\}. \tag{5}$$

In this connection by introducing the terms $\dot{e}_i$, the rate of transfer of currency of $[i]$, and $\dot{E}$, the rate of transfer from $[i]$ of other forms of money, m_i, the amount of currency, and M_i, the amount of other money in $[i]$ at time t, we have

$$\frac{d}{dt}\left(m_i + M_i\right) = \dot{r}_1^{(i)}$$

and the velocities of circulation, v_i and V_i of m_i and M_i, respectively, are defined by the equations

$$m_i v_i = \dot{e}_i, \; M_i V_i = \dot{E}_i$$

where

$$\dot{x}_1^{(i)} - \dot{r}_1^{(i)} = \dot{e}_i + \dot{E}_i = \sum_1^n p_j \dot{x}_j^{(i)}$$

Hence

$$m_i v_i + M_i V_i = \sum_{j=1}^n p_j \dot{x}_j^{(i)}$$

If we sum these equations for all i, and introduce suitable definitions of averages, we may write the usual *equation of exchange* (1)

$$mv + MV = \sum_{j=1}^n \sum_{i=1}^n p_j \dot{x}_j^{(i)} = \sum_{j=1}^n p_j (\dot{x}_j - \dot{r}_j) = T$$

If finally we denote the value of the right-hand member at $t = t_0$ by T_0, and write

$$mv + MV = PXT_0 \qquad (6')$$

then for any price index P there is determined the correlative trade index X by the equation

$$X = \frac{T}{PT_0};$$

e. g., if $P = \sum p_i \dot{X}_i / \sum p_0 \dot{X}_i$, $X = \sum p_0 \dot{X}_i / \sum p_0 \dot{X}_{0i}$.

3. Rather than follow this theory in more detail, which is the subject of much well-known work, let us pick from the general equations one or two special problems of interest. Suppose that the system is stabilized except for some particular commodity, so that fluxes and prices referring to other commodities may be regarded as constants, the disturbances of this commodity causing negligible perturbations in those others. If this industry is restricted to a single compartment [0][2] our equations (3) will reduce to two, one of them being the equation in the specific commodity, viz.—

$$\dot{x}_0 - \dot{r}_0 = \sum_{j=1}^n \dot{x}_0^{(j)} = \sum_{j=1}^n \left(a_j p_0 + b_j + h_j \frac{dp_0}{dt} \right) \dot{x}_j,$$

as an approximation; that is,

$$\dot{x}_0 - \dot{r}_0 = ap_0 + b + h\frac{dp_0}{dt}, \qquad (7)$$

where $a = \Sigma_j a_j x_j$, etc.; and the second one relating to the money flux through that compartment, viz.—

$$\dot{r}_1^{(0)} = p_0 \dot{x}_0 + \dot{E}_0' - \sum_{i=1}^{n} p_i (\dot{r}_i^{(0)} + f_i^{(0)} \dot{x}_0),$$

if we assume a specially simple case of the Stieltjes integral. For further simplicity we might suppose the $f_i^{(0)}$ linear in $\dot{x}_0$, and $\dot{E}_0' = 0$, so that

$$\dot{r}_1^{(0)} = p_0 \dot{x}_0 - (A\dot{x}_0^2 + B\dot{x}_0 + C) \tag{8}$$

This is the problem of the "dynamics of monopoly," already discussed in elementary fashion by the author.[3] A further special case occurs when $h = 0$, and yields the sort of monopoly investigated by Cournot.[4] An interesting extension could be obtained by considering certain of the coefficients, say b and C, as periodic functions of t. In the cases so far discussed π_ρ has been taken as the total profit $r_1^{(0)}(t_2) - r_1^{(0)}(t_1)$.

4. An exceedingly simple system, approximate to a Utopian monotony, is obtained by assuming that the ordinary integral parts of the Stieltjes integrals in (3′) do not appear, and that merely constant multiples of the $\dot{x}_j(t)$ remain. In this system we have

$$\dot{x}_i - \dot{r}_i = \sum_{j=1}^{n} f_i^{(j)} \dot{x}_j + \sum_{j=1}^{n} \dot{r}_i^{(j)},$$

n equations which may be solved for the $\dot{x}_1 \ldots \dot{x}_n$, if the determinant

$$\begin{vmatrix} 1 - f_1^{(1)} & -f_1^{(2)} \ldots & -f_1^{(n)} \\ \cdot & \cdot \quad \cdot \quad \cdot & \cdot \\ -f_n^{(1)} & -f_n^{(2)} \ldots & 1 - f_n^{(n)} \end{vmatrix}$$

does not vanish. Hence the π_ρ may be expressed in terms of the various r's and their rates of change—unused capitals and services. However, in a system where waste products are utilized when capital is fully employed, this false simplicity disappears, because it is precisely then that the determinant vanishes—for we must have $\dot{x}_i$ not all zero even when all the $\dot{r}_i$, $\dot{x}_i^{(j)}$ vanish. The extremal character of a π_ρ which was given in terms of these hoardings would not then determine the variable functions. On the other hand, it is precisely in such a system that we can condense the compartments into larger "compound" industries, and study first the large groups as compartments, then the parts of these, and so on, until the investigation becomes as minute as we desire.

5. In conclusion it may be remarked that the relation of economics to the calculus of variations is not accidental, nor the result of a generalization from previously found differential equations, since it is in the nature of an economic system that there should be a striving for a maximum of

some sort. In particular, equations of the type (3), such as the equation of demand (7), may in part be replaced by equations of the type (4).

[1] Irving Fisher, *The Purchasing Power of Money*, New York (1922).

[2] The corresponding problem for more than one compartment, in the case of competition, is discussed by C. F. Roos, in an article not yet published. Mr. Roos incidentally treats a hysteresis problem in which the functional character of (3′) is preserved.

[3] *Amer. Math. Monthly*, **31** (1924) pp. 77–83. Compare the fundamental hypothesis with the statistical study of Irving Fisher, *The business cycle largely a dance of the dollar, Quar. Pub. Amer. Statis. Assoc.*, December (1923).

[4] Cournot, *Récherches sur les principles mathématiques de la théorie des richesses*, Paris, 1838. See also G. C. Evans, *A Simple Theory of Competition, Amer. Math. Monthly* **29**, (1922), pp. 371–380.

SEPARABLE QUADRATIC DIFFERENTIAL FORMS AND EINSTEIN SOLUTIONS

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A quadratic differential form in n variables we shall call *separable* or *summable* if it can be reduced by any transformation of the variables to the sum of two forms, one involving only h of the variables, the other involving the remaining k variables, where $n = h + k$.

Such a form we shall call separable of type (h, k). We may of course have separable forms of type $(h_1, h_2, \ldots h_r)$ where $n = h_1 + h_2 + \ldots + h_r$. This means that the form can be reduced to the sum of r forms involving completely independent variables.

The various types for a given n are not necessarily mutually exclusive. There are possibilities of certain special forms belonging to more than one type.

If the form is euclidean it is of type $(1, 1, \ldots\ldots, 1)$ and vice versa this type is obviously euclidean. This is the extreme case of separability, the n-ary form being then transformable into the sum of n independent unary forms.

If $n = 4$, the possible types are

(a)	$(2, 2)$
(b)	$(3, 1)$
(c)	$(2, 1, 1)$
(d)	$(1, 1, 1, 1)$

We have examined the question: *When can an Einstein manifold be one*

of these separable types? For (*a*) we have shown[1] that there is one and only one solution, namely:

$$ds^2 = \frac{dx_1^2 + dx_2^2}{x_1^2} + \frac{dx_3^2 + dx_4^2}{x_3^2} \qquad (1)$$

For (*b*) we find that no solution exists, the proof being quite easy.

For (*c*) no solutions exist except of course those which are of the trivial euclidean type (*d*). Hence we have the theorem:

If an Einstein manifold is to be separable it must be either euclidean or else equivalent to (1). *This latter form defines an algebraic*[2] *manifold, namely a quartic spread of four dimensions imbedded in a flat space of six dimensions; the finite equations in six cartesian coördinates being.*

$$X_1^2 + X_2^2 + X_3^2 = 1,\ X_4^2 + X_5^2 + X_6^2 = 1. \qquad (2)$$

This is the intersection of two spherical hypercylinders.

The separability so far defined has been *complete.* There is another more general and more difficult theory of *incomplete or dependent separability* For example a form in four variables x_1, x_2, x_3, x_4, may in certain cases even though not separable in the first sense, be reducible to the sum of three binary forms

$$Q' + Q'' + Q''' \qquad (3)$$

where Q' involves only x_1, x_2, Q'' only x_1, x_3, Q''' only x_1, x_4. A special important case of (3) is

$$ds^2 = \alpha(x_1)dx_1^2 + \beta(x_1)dx_2^2 + \gamma(x_1)dx_3^2 + \delta(x_1)dx_4^2 \qquad (4)$$

Here $Q' = \frac{1}{3}\ \alpha dx_1^2 + \beta dx_2^2$, $Q'' = \frac{1}{3}\ \alpha dx_1^{2\prime} + \gamma dx_3^2$, $Q''' = \frac{1}{3}\ \alpha dx_1^2 + \delta dx_4^2$.

Einstein solutions of the above type actually exist and have all been determined elsewhere.[3] They may be represented as curved spaces of four dimensions immersed in flat space of 7 dimensions. The finite equations represent three surfaces of rotation with a common axis.

Every form in n variables is of course separable if we allow a sufficient number of forms in a smaller number of variables, provided the variables in the various forms added are not required to be independent. For example we may decompose the given form into the sum of not more than $\frac{1}{2}n(n+1)$ unary forms. We shall examine elsewhere the maximum number of binary forms that are requisite, and other generalizations.

[1] *Science*, **54**, 1921 (304–305); Geometrical theorems on Einstein's cosmological equations. *Amer. J. Math.*, **43**, 1921 (217–221); *Math. Ann.*, **85**, 1922 (227–236); also an article in press "An algebraic solution of the Einstein equations," *Trans. Amer. Math. Soc.*, **27** (1925).

[2] This means algebraic in finite form, not merely that the potentials g_{ik} are algebraic functions.

[3] Same references; also *Bull. Amer. Math. Soc.*, **27**, 1920 (62); and a detailed discussion in a forthcoming paper "Solutions of the Einstein equations involving only one variable," *Trans. Amer. Math. Soc.*, **27** (1925).

ON A NEW METHOD OF FACTORIZATION

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For numbers beyond the range of existing factor tables the problem of factorization is a very serious one, especially if nothing is known in advance concerning the character of the possible divisors. The most effective method so far invented is probably that used by Legendre (*Théorie des Nombres, 1797, p. 313*) which is based on the theory of quadratic residues and makes use of the fact that all numbers having a given quadratic residue contain only such prime divisors as belong to certain linear forms, tables of which have been given by Legendre for various residues less in absolute value than 100. Thus if -1 is known to be a residue the prime factors are all of the form $4n + 1$, and such numbers as 3, 7, 11, 19, etc., are ruled out as possible divisors; or if 7 is known to be a residue the prime divisors must be of the form $28n + 1, 3, 9, 19, 25, 27$. If -1 and 7 are both known to be residues these linear forms may be combined into $28n + 1, 9, 25$. Unfortunately the number of forms increases with the residue so that combining them is very laborious except for the smaller residues of the table. The larger residues are just as effective in excluding trial divisors, but they are often more trouble to use than they are worth because of the number of forms involved.

These serious difficulties may be avoided by replacing the tables of linear forms by stencils. The combination of any number of sets of forms is then accomplished by piling the corresponding stencils, one on top of the other. A large residue will be as easily used as a small one, and the list of possible prime divisors is given automatically and with very little chance of error. It is proposed to extend Legendre's table to include all numbers less in absolute value than 1000 which contain no square factors other than unity. The difficulty of finding suitable residues will thus be very much diminished. This will involve the making of some 1216 stencils, but the labor of making a stencil will not be great, and when complete the device will furnish a practicable means of handling any number less than 2,361,279,649, and will be of great service in dealing with numbers far beyond this limit.

Briefly the stencil method is as follows: Each stencil will have 100 rows and 50 columns, thus furnishing a cell for each of the 5000 primes from 1 to 48,593 listed on the first page of my List of Primes (Carnegie Institution of Washington, 1914). For any residue R a stencil is made by punching out a hole in each cell which corresponds to a prime which is of the proper linear form to have R for a quadratic residue. Thus for $R = -1$ a stencil will be made with holes punched in those cells which correspond to primes

which are of the form $4n + 1$ and for $R = 7$ those cells are punched out which correspond to primes of the forms $28n + 1, 3, 9, 19, 25, 27$. When these stencils are superposed the holes which shine through both stencils correspond to primes which belong to both sets of forms. The first stencil will shut out approximately one half the list of primes, and the second will shut out approximately half of those that remain; so that the discovery of as many as 12 residues will serve to exclude all but about 12 trial divisors for a number as great as the square of 48,593 or 2,361,279,649. For numbers of this order a sufficient number of quadratic residues less in absolute value than 1000 will not be difficult to obtain by well-known methods, the most effective of which is by expanding the square root of the number in a continued fraction.

A machine for cutting the stencils from the master-stencil is easily devised. The labor of proof-reading or of type-setting with all the errors involved in those operations is completely eliminated. The device has one very important advantage over a factor table in that while a factor table is of no service at all for a number just beyond its range the system of stencils will be very useful for numbers far beyond the limit indicated. Moreover, any additional information regarding the character of the factors is not difficult to make use of, which advantage is not enjoyed by other powerful methods such as the representation of the number by binary quadratic forms.

FUNCTIONALS OF CURVES ADMITTING ONE-PARAMETER GROUPS OF INFINITESIMAL POINT TRANSFORMATIONS[1]

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The purpose of this abstract is to study functionals of closed plane curves admitting one-parameter continuous groups of infinitesimal point transformations. Necessary and sufficient conditions are given. Extensions and generalizations of this invariant theory to functionals of closed plane curves depending in particular on a point on the curve and to functionals of $n - 1$ spreads in n dimensions are indicated.

The theory of functional invariants may be divided into two parts: one, which seeks functionals admitting one-parameter groups of *functional* infinitesimal transformations;[2] and another, the object of this paper, which seeks functionals admitting one-parameter groups of ordinary infinitesimal transformations.[3]

We consider a group of continuous transformations defined by

$$\frac{dx}{\xi(M)} = \frac{dy}{\eta(M)} = dt, \tag{1}$$

M denoting the variable point of the curve and t the parameter of the group of transformations; and $\xi(M)$ and $\eta(M)$ denoting real analytic functions of x and y.

Let $\Phi_n'[C/M]$ stand for the normal functional derivative of a functional $\Phi[C]$ of closed plane curves C taken at a point M on C; and let $\delta n(M)$ stand for the variation of the normal to the curve C (the inward direction considered positive). Assume the functionals $\Phi[C]$ to have a variation in the normal form

$$\delta\Phi[C] = \int_C \Phi_n'[C/M]\,\delta n(M)\,ds, \tag{2}$$

A necessary and sufficient condition that such a functional $\Phi[C]$ admit the group of transformations (1) is that

$$\int_C \Phi_n'[C/M]\,\delta n(M)\,ds \equiv 0 \tag{3}$$

for all closed curves C, where $\delta n(M)$ is obviously given by

$$\delta n(M) = [\xi(M)\cos(x, n) + \eta(M)\cos(y, n)]\,\delta t.$$

To get an explicit solution of the functional equation (3) we assume $\Phi[C]$ to be developable in an expansion

$$\Phi[C] = \varphi^{(0)} + \sum_{i=1}^{\infty} \frac{1}{i!} \int_6 \int_6 \cdots \int_6 \varphi^{(i)}(M_1, M_2, \ldots, M_i)\,d_{6_1}\,d_{6_2}\cdots d_{6_i}, \tag{4}$$
$$(i)$$

in which

$$|\varphi^{(i)}(M_1, \ldots, M_i)| < K^i \quad (K > 0) \quad (i = 1, 2, 3, \ldots.);$$

$\varphi^{(i)}$ is symmetric[4] in its arguments $M_1, M_2, \ldots, M_i$; d_{6_k} designates the element of area which corresponds to the point M_k, and 6 is the area within the closed curve C.

By functional analysis we can demonstrate the theorem:

THEOREM I. *If $\Phi[C]$ is developable in an expansion (4), then a necessary and sufficient condition that $\Phi[C]$ admit the group of transformations defined by (1) is that the $\varphi^{(i)}$'s in $\Phi[C]$ satisfy the linear partial differential equation of the first order.*

$$\sum_{j=1}^{i}\left\{\xi(M_j)\frac{\partial\varphi^{(i)}(M_1,\ldots,M_i)}{\partial x_j}+\eta(M_j)\frac{\partial\varphi^{(i)}(M_1,\ldots,M_i)}{\partial y_j}\right\}+ \tag{5}$$

$$+\varphi^{(i)}(M_1,\ldots,M_i)\sum_{j=1}^{i}\left[\frac{\partial\xi(M_j)}{\partial x_j}+\frac{\partial\eta(M_j)}{\partial y_j}\right]=0$$

$$(i=1,2,3,\ldots.)$$

Consequently we may assert that there always exist functionals of closed plane curves of form (4) admitting a given arbitrary continuous one-parameter group of transformations defined by (1).

The application of this general theory to the case of some of the more important groups (such as the projective and conformal) furnishes ample exercises in solutions of partial differentia lequations. We, however, note in passing that for area preserving groups the problem reduces to the solution of homogeneous partial differential equations.

The reader will have no difficulty in seeing that by means of one of Poincaré's classical theorems[5] conditions (5) can be interpreted in terms of absolute integral invariants in hyperspaces.

We have the following theorem which gives information as to the most general invariant $\Phi[C]$ of type (4).

THEOREM II. *If*

$$\Phi[C]=\varphi_0^{(o)}+\sum_{i=1}^{\infty}\frac{1}{i!}\int_{(i)}\cdots\int_{6}\varphi_0^{(i)}\ (M_1,\ldots,M_i)\,d_{6_1}\ldots.d_{6_i} \tag{6}$$

is a functional of closed plane curves admitting the group of transformations defined by (1) and if $I_i\ (M_1,M_2,\ldots,M)$ is the most general symmetric function of $M_1, M_2,\ldots,M_i$ which admits the group of transformations defined by

$$\frac{dx_1}{\xi(M_1)}=\frac{dx_2}{\xi(M_2)}=\ldots=\frac{dx_i}{\xi(M_i)}=\frac{dy_1}{\eta(M_1)}=\frac{dy_2}{\eta(M_2)}=\ldots=\frac{dy_i}{\eta(M_i)}=dt \tag{7}$$

$$(i=1,2,3,\ldots.),$$

then the most general functional of closed plane curves of the type (4) admitting the group of transformations defined by (1) can be written as

$$\Phi[C]=\varphi_{0\,0}^{(o)}+\sum_{i=1}^{i}\frac{1}{i!}\int_{(i)}\int_{6}\int_{6}\cdots\int_{6}I_i(M_1,\ldots,M_i)\varphi_0^{(i)}(M_1,\ldots,M_i)d_{6_1}d_{6_2}\ldots d_{6_i} \tag{8}$$

($\varphi_{00}^{(o)}$ being an arbitrary constant).

We can extend our theory to functionals $\Phi[C/M]$ of closed plane curves C depending in particular on a point M on the curve C (M itself of course

being subject to the transformation). Again for an explicit solution of our problem we assume $\Phi[C/M]$ to be of the form

$$\Phi[C/M]=\varphi^{(o)}(M)+\sum_{i=1}^{\infty}\frac{1}{i!}\int_{6}\int_{6}\cdots\int_{(i)}\varphi^{(i)}(M,M_1,\ldots,M_i)d_{6_1}\ldots d_{6_i}. \quad (9)$$

Then by a functional analysis similar to the one used for functionals of type (4), we can readily prove corresponding theorems to Theorem I and Theorem II.

The invariant theory of functionals of closed plane curves of types (4) and (9) can be generalized to functionals of closed spreads of $n-1$ dimensions embedded in the space of n dimensions. The reasoning involved in these generalizations is an obvious extension of the reasoning in the cases discussed in this abstract.

[1] The writing of this paper was suggested by Prof. G. C. Evans. Detailed proofs will be found in a paper to be offered to the *Transactions of the American Mathematical Society*.

[2] See papers by I. A. Barnett in these PROCEEDINGS, **6**, 1920, 200 and in *Amer. J. Math.*, **45**, number 1, Jan., 1923, 42; and also papers by the author in *Bull. Amer. Math. Soc.*, 30, number 7, July, 1924, 338 and in forthcoming issues of *Ann. Math. Princeton*, and the *Bull. Amer. Math. Soc.*.

[3] From one point of view the classical theories of integral invariants may be considered as a first chapter in this invariant theory.

[4] There is no loss of generality in making this assumption.

[5] H. Poincaré, *Méthodes Nouvelles De La Mécanique Céleste*, Vol. III, p. 41.

RESIN CANALS IN THE EVOLUTION OF THE CONIFERS[1]

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An outstanding characteristic of the Conifers as a group is the presence of canals producing turpentine and resin. These are present in the soft tissues or the wood in all Conifers with the sole exception of the genus Taxus. Since they are so universal a feature of organization, in this large and ancient group of plants, their evolutionary history has naturally been the subject of much discussion. The view generally held, at the present time, is that those Conifers in which the system of resin canals is most strongly developed, namely the Abietineae, represent the most modern and specialized forms. The geological history of Conifers, however, scarcely warrants such a conclusion however much it may harmonize with a purely philosophical interpretation of evolution as proceeding from the simple to

the more complex. Our knowledge of ancient groups of plants makes it tolerably clear, that in those forms, which are no longer dominant in our Earth's flora, the more complicated forms lie in the past rather than in the present. The Conifers are a group to which this general principle strikingly applies for they had their greatest development in the Mesozoic age.

In the living pine and its prototypes, in the Mesozoic, resin canals are present both vertically and horizontally, and form a continuous system in wood and bark, which is commonly tapped for turpentine and resin. In the higher members of the pine family, the hemlock and the fir, these canals disappear in the wood but are still prominent in the soft tissues. An interesting fact, in this connection, is that resin canals are always present in the wood of the root in the higher Abietineae. Another interesting situation which has been developed by the present author, is the occurrence of resin canals as a consequence of injury. This phenomenon has been shown to be present by the author in the four genera Tsuga (the hemlock), Abies (the fir), Pseudolarix (the golden larch of China) and Cedrus (the cedar of Lebanon, the Deodar, etc.). The cedar of Lebanon, and other species of the genus, are characterized by the occurrence of both vertical and horizontal resin canals following injury. In the other genera cited above, only vertical canals result in living species from injury. It is of interest, in this connection, to note that Cedrus has the oldest geological record of any of the four genera occurring as it does, in the Argonne in France, in the Cretaceous cliffs of the south of England, and in our own Potomac formation. A very interesting fact has developed in the case of the genus Abies from the American Miocene. Some years ago, the present author described a wounded wood, which was excavated in the construction of a tunnel, through the Sierra Nevada mountains, underneath sixty feet of conglomerate. This extinct form was characterized by resin canals, both in the horizontal and vertical planes. A figure of this interesting and important specimen is herewith introduced. It will be seen by examining the photograph, fig. 1, that resin canals of a small size appear in transverse sections, while a larger one can be seen in horizontal section. It thus follows that the firs of earlier date gave a wound-reaction, more like that of the very ancient genus Pinus, than do the modern species of Abies.

Another interesting feature of living pines is the presence of horizontal tracheids accompanying the rays. These are absent in certain of the higher Abietineae, notably the firs, but may be recalled by injury precisely as is the case with the resin canals just described.

A large and important sub-tribe of Conifers is the Cupressineae, using that term in its broadest sense. In these, the seed-bearing cone shows a simpler structure than does that of the Abietineae and resin-canals are absent in the wood. Perhaps the most interesting and ancient of the Cupressineae, in the broad sense, is the genus Sequoia, which has as its

surviving representatives, the Big Tree and the Redwood, both occurring west of the Rocky Mountains. Some years ago, the author pointed out that the two surviving species of Sequoia are both characterized by wound resin canals, fig. 2. In the Big Tree, resin canals also occur normally in the first year's growth, fig. 2, apparently in harmony with the principle of recapitulation. It has been shown by investigations, in the author's laboratories and elsewhere, that marginal ray tracheids may be recalled, not only in Sequoia, but also in other genera of the Cupressineae. The most interesting feature of the wound-reaction of Sequoia is found, however, in its more ancient representatives. Sequoia, in the Tertiary, shows the same reaction to wounding as do the surviving genera. In the Laramie Cretaceous, however, it is clear from investigations carried on by Dr. R. E. Torrey that this genus,[2] which here makes its first authentic appear-

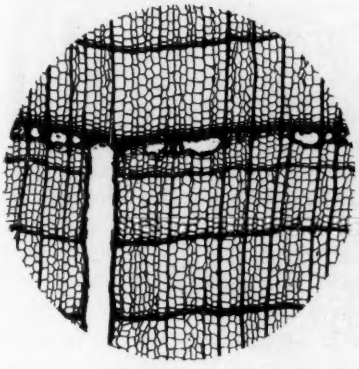

FIGURE 1

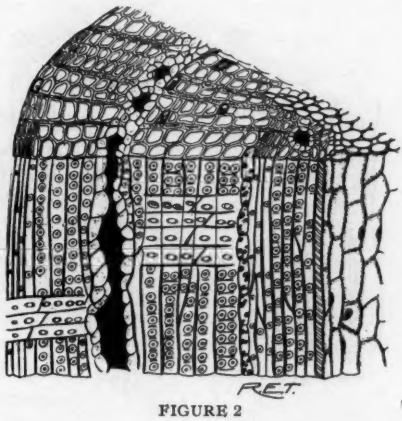

FIGURE 2

ance, is characterized in a number of species by traumatic resin in canals, both vertical and horizontal, fig. 3. In other words, the experimental evidence in the case of Sequoia, indicates clearly that it has come from pine-like ancestors and that in its more ancient representatives the resemblance to the pine in its wound responses, becomes more and more marked. The conclusion has been drawn by the present author, from these data, that the Cupressineae in a large sense are evolutionary derivatives of the pine.

Another very important sub-tribe of the conifers is the Araucariineae, a group at the present time confined to Australasia and South America, but formerly flourishing in very great abundance through the Northern Hemisphere. It is commonly assumed that the Araucarian Conifers are the most ancient and connect that group with Palaeozoic times. Anatomical and experimental investigations, however, are far from justifying any such conclusions. The present writer has described a number of Araucarian forms,

which have a wound-reaction like that of Sequoia and the firs, for resin canals make their appearance as a consequence of traumatic stimulation. This situation has been the subject of much discussion on the part of European investigators, who have questioned, without exception, the validity of the writer's conclusions. European palaeobotanists assume that the undoubted presence of wound resin canals in the case of supposed Araucarian Conifers removes them from the category of Araucariineae, and transfers them to the Abietineae. The writer and his students have established a number of genera of Araucarian woods of different types with Abietineous wound-reactions. The Europeans have recently transferred these wholly to the Abietineae, claiming that they represent a stage in the evolution of the Abietineae from Araucarian ancestors. Figure 4 shows a diagrammatic

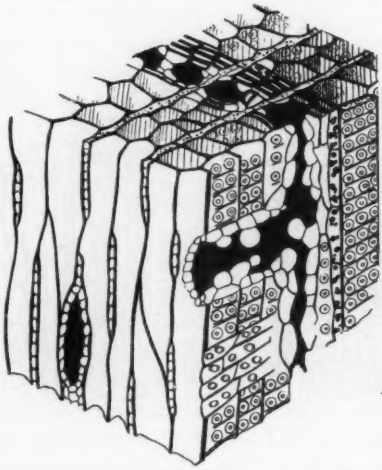

FIGURE 3

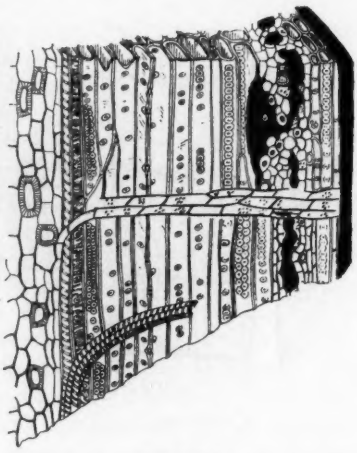

FIGURE 4

representation of the wounded wood of Brachyoxylon. The resin canals are represented as filled with black contents and obviously run only in the vertical direction.

Although the later Mesozoic woods with Araucarian structure and Abietineous wound-reactions have wound canals only in the vertical plane, those of lower geological range, namely, the Infracretaceous and Jurassic, have both vertical and horizontal wound canals, precisely as is the case with the older representatives of Sequoia and Abies. If logic prevails in this instance, we are compelled to conclude that the older Araucarian Conifers are nearer the Abietineae than the modern forms and that they are derived from the Abietineous stock. The European palaeobotanists conclude otherwise, and have recently transferred a host of woods formerly regarded

as undoubtedly Araucarian, from the Araucariineae to the Abietineae. As a result, we have a very interesting situation. The strongest argument for the antiquity of the Araucarian Conifers has been the supposed great abundance of their woods in the later Mesozoic. By the removal of practically all woods formerly regarded as Araucarian to the Abietineae, this argument becomes without force.

The general situation is of considerable interest. The higher Abietineae, the lower Cupressineae, and a large group of Conifers, until very recently unanimously considered to be Araucarian, all independently present wound-reactions indicating affinity with the very ancient genus Pinus. The logical conclusions is obviously to regard the higher Abietineae, the Cupressineae and the Araucariineae, all as offshoots of the Abietineae. If one adopts on the other hand, the view in vogue in Europe, one has to suppose not only that the higher Abietineae have produced the very ancient Pinus; but also that the Cupressineae have independently given rise to pine-like forms and finally that the same conclusion is to be adopted in the case of the Araucarian Conifers.

The only large group not considered in the above statement are the Taxads or yew-like Conifers, at present mainly confined to the Southern Hemisphere. The author is, at the present, endeavoring to secure material of these forms in the strata of their present seats. Should the experimental evidence in their case lead to the same conclusions as in the Abietineae, Cupressineae and Araucariineae, it will be scarcely possible for the European anatomists to continue to maintain their present illogical position. The resemblance of the lower Podocarps and Yews to the Abietineae is striking, even in their modern representaives, and the study of their fossil forms along experimental lines should prove of fundamental importance from the standpoint of the doctrine of descent.

[1] Investigation prosecuted with the aid of a grant from the Elizabeth Thompson Science Fund.

[2] The comparative Anatomy and Phylogeny of the Coniferales. Part 3.—Mesozoic and Tertiary Coniferous Woods, *Memoirs Boston Soc. Nat. Hist.*, 6, Number 2, April, 1923.

THE ORIGIN OF PARENCHYMA IN GEOLOGICAL TIME[1]

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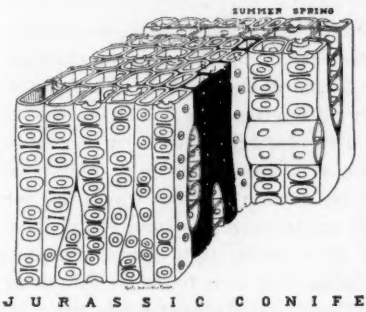
The author has devoted much attention to the study of the wood of extinct Conifers and other fossil trees. The data so acquired, extend over a long range of geological time, and throw remarkable and interesting light on the evolution of woody structures in plants. As is well known, the main organization of the secondary wood, in Conifers and in most other Gymnosperms, is composed of water-conducting elements known as tracheids. Primitively, the wood consisted entirely of elements of this character not only in the case of the secondary wood, but also in the oldest known trees in that of the primary wood as well. Later, the exclusively tracheary character of the wood gave place to one in which storage elements were developed side by side with water-conveying cells. In the primary wood, this condition was already well established in the Palaeozoic for lepidodendroid trees. The same statement holds for horizontal storage elements or rays in the Palaeozoic, for these made their appearance in the earliest known arboreal Lycopods. There is good reason to believe that in both these cases, namely, in the longitudinal storage elements of the primary wood and in the horizontally developed storage rays of the secondary wood, the food-storing cells have been derived from what were originally water-conducting elements or tracheids. The writer has developed this hypothesis on the basis of the anatomical organization of the primary and secondary wood, in the case of the Lepidodendroids, in his work entitled, "The Anatomy of Woody Plants."[2]

In the present preliminary article, it is proposed to discuss the origin of the storage elements of the secondary wood, which appeared in later geological times and which have a vertical position in the wood, in other words, the wood parenchyma. Not only have living Conifers been extensively studied in this connection, but also the very important Mesozoic forms have been examined so far as opportunity permitted. It is believed that the data thus obtained, throw an interesting light on the general process of evolution of wood, that most important and continuous of all biological documents.

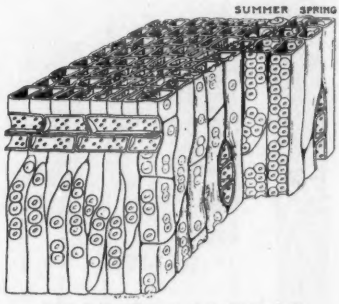
So far as we are informed, the woods of the earlier Mesozoic were without longitudinal storage elements or wood parenchyma. The author has examined abundant material from the Triassic of Arizona, the Connecticut Valley, the Bay of Fundy and the Rhaetic of Sweden, and in no case has he found any indication of the presence of longitudinal storage elements in the secondary wood. In this respect the Triassic forms closely correspond

with those of the Palaeozoic period, which in the present state of our knowledge, were entirely without wood parenchyma. It is only in the Jurassic that we begin to find indications of the occurrence of longitudinal storage cells in the secondary wood of Conifers. Fig. 1 shows the organization of part of two annual rings in a Conifer from the Jurassic of Brora, in Scotland. On the left appears the end of the summer wood. On the right are represented the spring tracheids. It will be noted that at the end of the summer wood, there are elements represented black in the illustration which differ from tracheids, not only in the chemical character of their walls, but also by the fact that they are short, square at the ends, and provided with simple instead of bordered pits. The position of these elements, which are parenchyma cells at the end of the year's growth, is apparently significant. This location enabled them to supply food to the reawakening cambium at the beginning of the new period of growth. It is an interesting fact, that the bordered pits of the terminal tracheids of the



JURASSIC CONIFER

FIGURE 1



TELEPHRAGMOXYLON

FIGURE 2

annual ring show a similar adaptation, since they are directed radially on the terminal tracheids only, having an exclusively tangential orientation in the earlier tracheids of the year's growth. It was long ago suggested by Strasburger that the tangential pitting of the terminal summer tracheids, in Conifers, is for providing the cambium with an abundant supply of water. In older woods, this tangential pitting does not occur, but it is apparently of earlier origin than the longitudinal parenchyma.

A very interesting Mesozoic wood, which we have diagrammatically represented in figure 2, carries the question of the origin of wood parenchyma a step further back. By inspecting the figure, it will be seen that certain of the tracheids at the end of the summer's growth, although provided with bordered pits on their tangential as well as radial walls, as is normal for the summer tracheids, present a striking peculiarity by reason of the fact that they are transversely septate. This remarkable and inter-

esting wood is discovered by Dr. R. E. Torrey, in working up material collected by him, from the Mesozoic of the Western and Southern States.[3] It has been suggested by Dr. Torrey that this condition represents the first stage in the origin of wood parenchyma, in the manner earlier described by the present author in his "Anatomy of Woody Plants," cited above. Professor Torrey expresses the opinion that the transverse divisions in the terminal tracheids of Telephragmoxylon facilitate the laterial diffusion of water through the bordered pits, a condition obviously advantageous to the cambium. This discovery, as it pointed out by the author under discussion, goes far to confirm the theory of the origin of wood parenchyma earlier advanced by the present writer.

Obviously, the next stage in the evolution of parenchyma in the secondary wood is one in which certain of the divisions of the septate tracheids retain their protoplasm and fail to become lignified, in other words, become typical parenchyma cells. At the same time, these elements lose their bordered pits and acquire the simple spores, which characterize living storage cells. Figure 3 represents, in a diagrammatic fashion, the stages in the origin of wood parenchyma from tracheids. The tracheid on the left represents the normal organization of a summer tracheid, in a Mesozoic or modern Conifer, which has pits both on its tangential and radial faces. The next to the right shows a septate tracheid, such as is found in Telephragmoxylon. The third towards the right illustrates the transformation of certain of the septations into parenchyma cells, with simple pits, cellulose walls and persistent protoplasm. This illustration corresponds with the course of evolution, as is shown by the organization of the wood of the root in the living spruces (Picea). Here one finds septate tracheids partly consisting of short tracheids and partly composed of true parenchyma cells. The illustration to the extreme right, in the figure under discussion, shows the entire transformation of a tracheid into parenchyma cells, the condition found in most living Conifers and in all Dicotyledons. Curiously enough, even in the most advanced Conifers and also in certain Dicotyledons, one gets transitions from septate tracheids to parenchyma cells as a consequence of injury, a clear example of reversion to an ancestral condition.

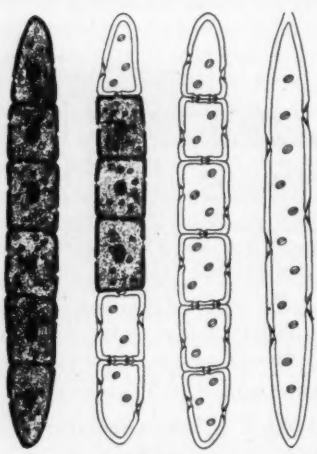


FIGURE 3

Figure 4 represents, somewhat diagrammatically, the mode of occurrence

of parenchyma in the wood of the root of the spruce. It will be seen by inspecting the figure that the end of the year's growth consists partly of tracheids, partly of septate tracheids, and partly of true parenchyma cells. This condition is found only in Picea and Pseudotsuga. In the larch, the fir and the hemlock, as well as other higher members of the Abietineae, the terminal parenchyma shows no indication of derivation from septate tracheids. The only exception to this statement occurs in woods which have been subjected to injury. In these, one still finds transitions from parenchyma cells to tracheids.

In the mass of Conifers and in practically all Dicotyledons, wood parenchyma is not confined to the end of the year's growth, but is distributed throughout the annual ring. Certain of the pine family present an interesting transitional condition in this respect. For example, Tsuga, although

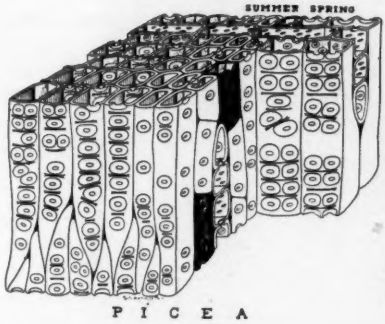


FIGURE 4

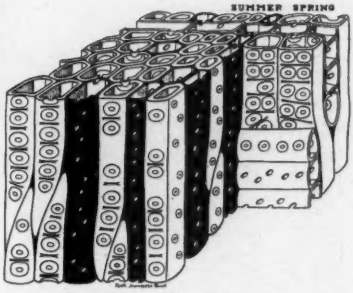


FIGURE 5

generally provided with terminal parenchyma only, occasionally exhibits longitudinal storage elements distributed throughout the annual ring. This condition is diagrammatically represented in figure 5. It will be clear to the reader that in this illustration, not only are the parenchyma cells present throughout the annual ring; but they show no normal transition to tracheids, other than the fact that they occur in longitudinal series, which have the general shape of tracheary elements. In the cypress-like Conifers, this condition becomes universal. Investigations carried out in the writer's laboratory on the Yews and Araucarians, make it clear that these important groups of Conifers formerly possessed wood parenchyma distributed throughout the annual ring, although at the present time they have, for the most part, lost it. The Dicotyledons in general resemble the higher Conifers, in having parenchyma cells distributed throughout the annual ring and showing, under normal conditions, no transition towards tracheids other than the general conformation of the series of parenchyma cells which resemble, in shape, tracheids.

The conclusion is reached, as a result of a study of living and extinct Gymnosperms, that storage parenchyma has been derived from tracheids. It is further clear that it made its appearance first at the end of the annual ring, and in this position shows most clearly its tracheary origin, often manifesting every gradation towards tracheary elements. The terminal position is doubtless correlated with the necessities of the cambium as regards nourishment. Later, the parenchyma elements became diffused throughout the annual ring and no longer showed transitions towards tracheids. It is of interest, in this connection, to note that Palaeozoic Gymnosperms were equally without annual rings and wood parenchyma. The evidence further indicates that the appearance of wood parenchyma is definitely coördinated with the development of annual rings, which in turn are the result of progressive refrigeration of the surface of our globe, in later geological times.

[1] Investigation prosecuted with the aid of grant from the Elizabeth Thompson Science Fund.

[2] The University of Chicago Press, 1917, pages 37–39 and 61–64.

[3] Torrey, R. E., "Telephragmoxylon and the Origin of Wood Parenchyma," *Annals Botany*, **35**, No. 137, January, 1921.